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(54) Title: METHOD FOR PRODUCTION OF FLEXIBLE PANELS OF HYDROPHOBIC AEROGEL REINFORCED WITH FIBRE FELTS

(57) Abstract: This invention describes a method for producing large pieces of aerogel. A felt of fibres is added to the silica solution, which is prepared from a trialkoxysilane (methyltrimethoxysilane and methyltriethoxysilane). The most relevant aerogel properties produced with these trialkoxysilanes are flexibility, low density, low thermal conductivity and hydrophobicity; these properties are kept from cryogenic temperatures up to at least 350°C. Felts are used to improve the mechanical strength of aerogels, allowing the manufacture of pieces with large dimensions, which has been a major limitation for the application of these materials. The applications of the material described herein include thermal insulation for the construction, oil and gas, cryogenics, thermoelectric, aeronautics and space sectors. However, due to high specific surface area, this material is also important for applications in pharmaceuticals and wastewater treatment.

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DESCRIPTION**METHOD FOR PRODUCTION OF FLEXIBLE PANELS OF HYDROPHOBIC
AEROGEL REINFORCED WITH FIBRE FELTS**

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Field of invention

Aerogels offer unique physical properties for
15 thermal and acoustic insulation due to their very low
thermal conductivity and high porosity. Aerogels are
generally used to minimize heat transfer by conduction and
convection. Other properties, namely hydrophobicity, help
extending the applications of those materials. Concep-
20 tually, aerogels can be used in numerous applications
involving heating and cooling, particularly in buildings,
industrial equipment, satellites, launchers and pipelines.
However, characteristics such as size and flexibility and
production costs have limited utilization of aerogels,
25 making the preparation of monoliths a considerable
technical challenge for large-scale production. Numerous
attempts have been made to improve the performance and
maturity of the manufacturing process. This invention
relates to a process for the production of silica-based
30 composite aerogels that also contain fibres in the form of
felt panels. This invention discloses a method for
producing aerogel flexible panels that can be used for
thermal insulation in the building, oil and gas,

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5 cryogenics, thermoelectric, aeronautical, and space
sectors. Other applications of this type of composite
aerogel panels include aerosols controlled adsorption,
separation of hydrophobic and hydrophilic species, as well
as selection of specific chemical functionalities. The high
10 specific surface area of aerogel is attractive for
catalysis applications, removal of pollutants from water,
controlled release of active species, as well as filtration
and percolation of liquids in porous media.

15 **State of the art**

Aerogel is a porous lightweight synthetic
material derived from a gel in which the liquid component
of the gel is replaced by a gas, resulting in a solid with
20 extremely low density and thermal conductivity. The first
aerogels were synthesized from silica gels and offered
unique properties of thermal and acoustic insulation.
Initially, aerogels were produced in a granular form and
their development was slow because of the time and labour
25 required to complete the process, in addition to other
technical difficulties. The technologies for aerogel
production have been strengthened in recent decades, being
reflected in the growing number of patents and the
importance and diversity of applications. Silica aerogel, a
30 substance derived from a silica gel, is the most common
type of aerogel and the one most studied and applied in a
systematic way. However, other materials such as carbon,
alumina, titania, zirconia, resorcinol-formaldehyde, and

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5 chalcogenides have been used in the development of aerogels to obtain specific properties. The present invention relates to a method and process for producing silica-based aerogels.

10 Several methods have been investigated for aerogel synthesis. Aerogels are sol-gel materials dried carefully to avoid collapse of the pores, creating a solid porous nanostructure with porosity higher than 90%. High porosity leads to some unusual physical properties. For
15 example, silica aerogels can be made with low thermal conductivity ($\sim 20 \text{ mW m}^{-1} \text{ K}^{-1}$), high surface area ($\sim 1000 \text{ m}^2 \text{ g}^{-1}$) and low density ($\sim 50 \text{ kg m}^{-3}$). Some aerogel properties, particularly chemical (composition, reactivity, hydrophobicity), thermal (conductivity, heat capacity, flammability),
20 lity), structural (Young's modulus, tensile strength, elastic strain limit), optical (luminescence, transparency), acoustic (speed of sound, absorption) and electrical (conductivity, polarization, magnetic susceptibility), are often unique in the field of synthetic
25 materials. Silica aerogels can be prepared by various processes, typically comprising four stages: (i) gelation, (ii) aging, (iii) washing, (iv) drying. The first stage involves gelation, i.e. the condensation of one or more silicon precursors to form a matrix based on silica by sol-gel chemistry. The pores of the matrix are filled with
30 reaction by-products and solvent. Gelation is defined as the process corresponding to the transformation of a polymeric or colloidal suspension in a solid permeated by a

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5 liquid through continuous formation of a porous three-dimensional solid network, which is uniform throughout the whole solvent and without formation of any precipitate. In the second phase we proceed to the aging of the multiphase structure of the gel. Aging is the process in which the material is maintained for a predefined time under controlled environmental conditions, while slowly varying the characteristics of the material. In case of gels, aging is a curing period in which the structure is immersed in a liquid mixture, to obtain a strong solid structure. The third stage includes washing the gel that is an optional step. This step can be used to remove salts or other components from the structure used in the reaction and, in many cases, to replace the solvent in the interior of the solid network by another network that facilitates the subsequent step. The last phase, drying, involves solvent extraction without causing the collapse of the structure, leaving the silica nanostructure intact. Drying may be achieved by freezing, at ambient pressure (evaporative drying), or using supercritical fluids. The invention essentially describes a sol-gel process, starting from the precursor methyltrimethoxysilane (MTMS) or methyltriethoxysilane (MTES) for synthesizing a silica gel and preparing flexible aerogel large monoliths with superior thermal insulation characteristics. The reinforced aerogel structure is produced through the incorporation of a felt of fibres.

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5 Aerogels have been used for multiple applications, from space to terrestrial applications, to preserve heat or cold, remove moisture, and make cosmetics. Hundreds of patents and utility models about methods, processes, and applications of aerogels are known.

10 Solutions involving aerogel have been used for fire protection and as flame retardant (e.g. CN101357852, CN102531536, and CN102634351), as well as art and decoration (GB932211). Although most patents mention synthetic ingredients, a method using rice husk ash as raw

15 material for the preparation of SiO₂ reinforced aerogel has been proposed (WO2013010371). Composites involving substances such as manganese, alumina-titania or polyurethane powder have been proposed (CN101281821, CN1749214, GB1345944, GB761808, GB788151, and GB955275). Transparency

20 and other optical properties of aerogels were used to optimize the propagation of optical signals, namely in lighting devices (e.g. JPH11314940 and JP2000182420). A wide variety of natural and synthetic fibres have been added to improve the mechanical properties and developing

25 specific technologies (e.g. CN202597930 and KR20100083543). Aerogels were also used in filament coatings, namely for elastomers (GB1159063 and GB1345944), and proposed for encapsulation applications (e.g. processors), casting (e.g. motors), and multilayer insulation (GB821822, GB980109, and

30 WO2011119745). However, thermal and acoustic insulation are the most common applications of these materials (e.g. CN101698584, DE102009033367, KR100864784, KR20110082379, US5973015, and US6087407). Aerogels have been used in the

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5 field of electronic and electromechanical parts, including engines (GB1247673 and GB1433478) and engines coating (EP0041203). Electromechanical applications (e.g. for power supplies) have also been developed (EP0814520, EP0875950, US5948464, and US6148503). Indeed, applications can be very
10 diverse and these materials were even developed for special niches, including metamaterials (CN102531519), shape memory alloys (US20100144962 and WO2008057297), and endoscopes (JP2000107121). Because of unique properties of certain hydrophobic aerogels, various technologies for humidity
15 control and environmental monitoring have been disclosed (e.g. US4871607). The demand for advanced functional materials with improved thermal and structural properties is growing. Aerogels are undoubtedly among the most suitable materials for thermal insulation due to their low
20 thermal conductivity. Concerning structural properties, aerogel solutions are substantially less efficient. For this reason, structural properties somehow limit the applicability of aerogels solutions for thermal insulation. There are many patents and utility models describing
25 methods, processes and technologies to produce and apply aerogel. Patents that to some extent relate to the present invention are: CN101698584, CN1749214, JPH0834678, KR100831877, KR20100053350, KR20100083543, KR20100092683, KR20110082379, US5973015, and US6087407. Patent
30 KR20100053350 discloses a method for manufacturing aerogel blankets. The purpose of the invention is the manufacture of aerogel blankets that provide better insulation. The process utilizes tetraethylorthosilicate (TEOS) as precur-

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5 sor and fibres to improve elasticity at a large scale. Patent KR20100083543 discusses a method of manufacturing insulating silica aerogel blankets at high temperature, including fibreglass fillers. This method includes crushing a felt of specific fibres (e.g. glass or carbon),
10 application of a non-solvent organic type of adhesive, and subsequently adsorption of a silica aerogel powder by the thin layer of fibres. An insulating, multilayer, laminated material is then obtained. Patent KR100831877 discloses a method for the preparation of monolithic silica aerogels,
15 which is obtained by drying at normal pressure from the hydrolysis mixture of a precursor of organically modified silicon methanol and oxalic acid. The mixture can contain one or more silanes and preferably comprises MTMS ($C_4H_{12}O_3Si$). This method for the preparation of silica
20 aerogel monoliths also results without adding any fibres. The material produced is soft and flexible, but also brittle. Patent KR20100092683 discusses a method of manufacturing a flexible silica aerogel. The material is produced through a drying process with carbon dioxide in a
25 supercritical state. The mixture of solutions containing MTES or TEOS is used to produce small plates of flexible aerogel. Fibres are not included and the material is brittle. Patent KR20110082379 discloses a method for preparation of materials with a high degree of thermal
30 insulation based on fibres impregnated with aerogels. Mixtures of silica gel containing alkoxy silane and isopropyl alcohol are hydrolysed by adding acidic aqueous solutions. The polymerization reaction of the TEOS solution

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5 is favoured by addition of small amounts of a basic solution. The silica sol is impregnated into the fibres to produce flexible aerogels. The invention provides a translucent aerogel JPH0834678. To obtain a material with superior resistance, while preserving the ability of
10 insulation, the silica skeleton is reinforced with fibres. A well-structured and multilayer fabric is used to make translucent properties. The rigidity of the material obtained is significant. Patents US6087407 and US5973015 discuss a process for manufacturing flexible aerogel
15 composites with improved mechanical stability. The invention relates to a process for the production of aerogels based on organic, flexible, mechanically stable, polymeric condensates of formaldehyde and containing composites that are mixed with glass, carbon, aramid or
20 plastic fibres. Patent CN1749214 discloses a method for preparing composite aerogels for thermal insulation. The process involves the mixture of silicon oxides and titanium fibres, and supercritical drying. The invention requires the use of TEOS, ethanol, deionized water and ammonia with
25 well-defined molar fractions, as well as a vacuum impregnation process. A flexible, nanoporous silica material is obtained; the thermal conductivity is remarkably low ($15 \text{ mW m}^{-1} \text{ K}^{-1}$), but the density is unusually high for aerogel (130 kg m^{-3}). Patent CN101698584 describes
30 a method for preparing a silicon oxide aerogel structure that uses a felt for the purpose of mechanical reinforcement. The method comprises winding of felt, preparation of the silica solution, impregnating the felt,

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5 aging, surface treatment, and drying under supercritical conditions. The continuous fibre reinforcement can be selected from the following fibres: glass, aluminium silicate, carbon and basalt; organic felts can also be chosen. The preferred silicon alkoxide used in the process
10 is TEOS. The recommended solvent is ethanol or a mixture of ethanol and isopropanol. According to this method, large composite rolls can be made (e.g. 1×10 m). The surface treatment consists of trimethylchlorosilane (TMCS) in a solution of 50% ethanol for 32 h after aging at room
15 temperature for 24 h. Patent with reference US2012/046469 and the associated document WO2013/009984A2 discuss a method for producing porous gels from a silane and a catalyst solution. A non-supercritical drying of the gel delivers a porous material without elastic recovery. The
20 method is applied to alkyl-linked silanes; it is specifically claimed utilization of MTMS. Filler fibre (e.g. quartz or zirconia) or powder is used to improve the properties of the aerogel. However, this method does not claim the utilization of felts. The difference between
25 fibres and felts is relevant. Felt is a nonwoven fabric produced by braiding, compression, and condensation of fibres. The macro and micro structure of the felt is homogeneous and irregular, respectively. Aerogels produced by the method described in such document shrink about 5%,
30 with only small cylindrical samples described. Flexibility, particle shedding, and structural properties such as Young's modulus are not discussed. Nonetheless, documents CN101698584 and WO2013/009984A2 have the highest

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5 similarities to the method proposed in the present invention.

Increasing the size of the aerogel monoliths poses serious technical problems, which limits mass
10 production of aerogels. Presently, the major concern with regard to the production of silica aerogels include high fragility, deformation and shrinkage during drying, limited flexibility, small size, significant particle shedding, complex manufacturing process and high production costs;
15 these issues affect competitiveness of aerogel solutions. Numerous attempts have been made to improve the added value and maturity of the manufacturing process. To some degree, fibres (e.g. glass fibre) have been introduced in composite materials to enhance the mechanical properties of the
20 aerogel. To minimize the aforementioned problems, various types of continuous and discontinuous fibres, felts, and fabrics have been used to overcome specific problems. Although most inventions are dedicated to offer individual solutions to these problems, there are no patents examining
25 the technical issues in an integrated manner. The present invention addresses these problems simultaneously and provides a methodology for mass production.

Description of figures

30

Relevant aspects and expected advantages of the present invention are described briefly to accompany the detailed description. It also includes a table with

5 relevant physical properties of the composite aerogel. To facilitate the understanding of the proposed method, the following figures are included:

Figure 1 illustrates the process of producing composite
10 aerogels, where the sol solution (1) is poured from a container (2) into a tray (3) containing a felt matrix (4).

Figure 2 shows an image obtained by scanning electron
15 microscopy with the aerogel impregnated in the fibre felt.

Figure 3 shows a plot of thermogravimetric analysis where the weight loss is plotted as a function of temperature.

Figure 4 presents the stress vs. strain curves of the
20 aerogel composite before and after immersion in liquid nitrogen.

Table 1 shows physical properties of aerogel composites described in the document.

25

Summary of the invention

Silica-based aerogels possess remarkable properties for various applications. However, the applicability
30 of these materials has been limited by the difficulty of making them in larger dimensions. This problem is mainly due to the fragility of the materials; a process suitable to improve the mechanical strength of aerogels is addition

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5 of fibres. In the present invention it is used a felt based
on silica-fibres to improve the mechanical properties of
aerogels prepared from MTMS and MTES. This felt, which is
flexible and low density, has fibres arranged uniformly,
allowing a homogeneous distribution of the fibres in the
10 final composite material. Additionally, the felt has high
thermal and mechanical resistance.

The aerogels prepared with MTMS and MTES
precursors show very interesting properties, namely high
15 flexibility, very low density and thermal conductivity, and
are also hydrophobic. However, large scale production was
not possible without additional components that allow for
mechanical strength improvement. Thus, this invention uses
a felted fibre of silica and a solution ('sol') prepared
20 from the hydrolysis and condensation reactions of the above
precursor solutions.

The synthesis process of the final composite
material is fairly simple. In a first step the solution is
25 prepared using a silica precursor, aqueous solutions of
acid and basic catalysts, and an organic solvent.
Subsequently, this 'sol' is added in a tray containing the
felt, which fits the internal dimensions of the tray. After
a few hours a gel is obtained. This gel is kept for a day
30 or more in the same conditions of pressure and temperature
to strengthen its solid structure, and the gel is finally
dried in an oven at ambient pressure, and subjected to
various temperatures between 60 and 200°C.

5

The final aerogel composite has the internal volume of the tray where it is prepared and can have different dimensions, depending only on the size of the tray and the oven where drying occurs. The thickness of the aerogel composite can vary between 1 and 4 cm. Since the thickness of the fibres felt is between 5 and 15 mm; to increase the thickness of the final composite material, multiple layers of felt are superimposed on each other. In this case, several layers of felt are sewn to prevent felt layers from separating from the aerogel composite. For sewing several layers of felt, a line with high thermal resistance is used.

The process presented in this invention allows for production of large flexible panels of aerogel with low density and thermal conductivity, hydrophobic, and an operating temperature range from cryogenic temperatures up to at least 350°C. In the detailed description we summarize some of the properties of the resulting material, as well as a detailed description of the manufacturing process of the aerogel composite.

Detailed description of the invention

Exceptional properties of aerogels such as low density, low thermal conductivity and good performance under extreme temperatures make them appropriate for numerous applications, e.g. building insulation, aerospace

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5 devices, cryogenics, etc. However, their applicability has been limited by the difficulty of preparing these materials in large dimensions, without degrading the structural properties. The present invention overcomes some limitations of these materials, since it describes a way to
10 prepare large pieces of aerogel, maintaining the relevant physical characteristics. For this purpose, the present aerogel synthesis process uses the precursor MTMS, which yields superior properties such as flexibility and hydrophobicity, and is also suitable over a wide range of
15 temperature, from cryogenic temperatures up to at least 350°C. This synthesis process is described in some patents and scientific literature (KR100831877; Rao et al., "Synthesis of silica aerogels using Methyltrimethoxysilane (MTMS) precursor", J. Colloid Interface Sci. 300, 279-285,
20 2006; Durães et al., "Tailored silica based xerogels and aerogels for insulation in space environments", Adv. Sci. Technol. 63, 41-46, 2010). However, the resultant material is very brittle; increasing the aging time is not sufficient to strengthen the structure and enabling
25 preparation of large samples. In order to overcome the structural fragility of aerogels prepared with MTMS precursors, in the present invention, a felt of silica fibres is added (Figure 1). The felt has very low bulk density ($<20 \text{ kg m}^{-3}$) and the fibres are laid homogeneously
30 at a macroscopic scale. The homogeneous distribution of fibres in the felt also ensures fibres uniformity in the final product. Since the felt possesses high mechanical and thermal resistance along with low density, the addition of

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5 this felt maintains low density, flexibility and hydrophobicity, but improves the mechanical strength of aerogels prepared from trialkoxysilanes. Furthermore, addition of this felt allows for the preparation of highly flexible aerogels with large dimensions.

10

Generally, the process of synthesis of silica aerogels comprehends three main stages: (A) preparation of a gel by hydrolysis and condensation reactions of a precursor, (B) aging, while condensation processes are
15 still ongoing, and finally (C) drying. For step (A) are necessary a precursor, a solvent, and an aqueous acid and basic catalyst solution. Precursors such as MTMS and MTES can be used. Aqueous solutions of oxalic acid and ammonium hydroxide are used as acid and basic catalysts, respectively.
20 The concentration of acid catalyst can vary from 0.001 to 0.1 M and the concentration of the base catalyst should be higher than 5 M. For the solvent, one or more organic solvents can be used, namely methanol and ethanol. The molar ratio solvent / precursor varies between 15 and
25 40. Up to 10% of a tetraalkyl orthosilicate (either TMOS or TEOS) can also be added as co-precursor. The solution obtained by adding the precursor, the catalyst, and the solvent is poured to a vessel containing the felt. The felt is trimmed according to the shape of the composite material
30 to be obtained in the end. The thickness of the felt varies between 5 and 15 mm and several layers of felt can be added to increase the final thickness. If several layers of felt are necessary, the felt should be sewn with kevlar,

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5 fibreglass, or other line of high thermal and mechanical
resistance. Needling prevents the various layers to
separate from each other in the final material.
Subsequently, the gel takes the shape of the container
where the sol was added. Depending on the application,
10 samples with specific dimensions can be prepared, e.g. from
250×250 mm with a thickness from 1 to 4 cm. The mass of the
felt with respect to the mass of the final aerogel
composite is always less than 15%. The size of the final
material is only limited by the size of the container used
15 in the production process. During step (A) the solution is
maintained in a controlled environment between 25 and 30°C.
After that, the gel obtained is kept between 1 and 4 days
under the same conditions of temperature in order to
strengthen the solid network (step (B)). Finally, the gels
20 are placed in an oven for drying at ambient pressure, being
subjected to multiple temperature cycles between 60 and
200°C that may last up to 2-9 days, depending on the
thickness of the gel to be dried (step (C)). For an aerogel
with reduced thickness (~10 mm), the total drying time is
25 significantly shorter than the time required for drying an
aerogel 40 mm thick.

Using precursors such as MTMS and MTES there is
very low chemical affinity between the solid and the
30 solvent network retained therein. This reduced affinity
between the components of the gel prevents the collapse of
the solid network during drying at ambient pressure. Thus,
it is possible to attain dried materials at ambient

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5 pressure with properties similar to those resulting from
supercritical drying. Drying with supercritical fluids
shows some disadvantages compared with evaporative drying
since this is a more costly process in terms of equipment
and consumables, and is also more dangerous due to the high
10 pressures involved.

Table 1 shows some aerogel properties resulting
from the present invention. The density of the resulting
material, $\sim 85 \text{ kg m}^{-3}$, is considerably low for a material
15 obtained by drying at ambient pressure. The thermal
conductivity measured at room temperature and pressure is
 $32 \text{ mW m}^{-1} \text{ K}^{-1}$ according to the EN12667 and ISO8302 stan-
dards. Both components used in this invention, the aerogel
and the felt are based in silica, which ensures structural
20 integrity of the final aerogel composite. The integrity of
the final material, which can be confirmed by the SEM
micrograph of Figure 2, leads to small particle shedding,
contrary to what happens with aerogels available in the
market. Additionally, due to the inorganic character of
25 both felt and aerogel, the material obtained in this
invention can be used up to at least 350°C . This is
confirmed from results by thermogravimetric analysis
(Figure 3), because the weight loss of the sample up to
 380°C is less than 5%. In order to also assess the strength
30 of this material at cryogenic temperatures, the aerogel
composite is soaked in liquid nitrogen. The aerogel
composite does not lose its flexibility after the cryogenic
fluid is evaporated. Figure 4 shows the curves of stress
vs. deformation of the aerogel composite before and after
35 immersion in liquid nitrogen. The flexural modulus before

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5 and after immersion in liquid nitrogen is 58.5 ± 3.3 and 40.1 ± 4.1 kPa, respectively. On the other hand, the material flexibility is maintained when the aerogel panel is wound and unwound on itself, with a radius of up to 2-3 times the thickness of the panel.

10

Another important property for many applications is hydrophobicity, which prevents material degradation caused by contact with water or humidity. The flexible aerogels resulting from this invention have a contact angle of ~ 140 degrees, hence confirming their high hydrophobic character.

The dimensions of the panel are limited by the length and width of the tray. Increasing in thickness does not significantly reduce flexibility of the material, but increases the drying time.

Table 1

Property	Value
Apparent density	84.73 ± 3.19 kg m ⁻³
Thermal conductivity	38.84 ± 0.48 mW m ⁻¹ K ⁻¹
Modulus of elasticity (flexural mode)	58.5 ± 3.3 kPa 40.1 ± 4.1 kPa (after liquid N ₂)
Contact angle	142.87 ± 7.92 degrees
Loss of mass as a function of temperature	< 5% up to 380°C
Shrinkage	< 1%
Particle shedding	< 6%

35

5

CLAIMS

1. A method to produce large, hydrophobic, flexible panels made of silica aerogel composites reinforced with fibres, the method comprising:

- a) Preparation of a precursor solution based on methyltrimethoxysilane (MTMS) or methyltriethoxysilane (MTES);
- 15 b) Optionally, addition of a tetra orthosilicate - tetramethylorthosilicate (TMOS) or tetraethylorthosilicate (TEOS) - up to 10% measured in terms of the initial number of moles of silicon in the solution;
- c) Catalysis of the precursor solution in two steps, one 20 acidic and one basic;
- d) Addition of fibres with concentration lower than 15% by weight in the final composite;
- e) Pouring the precursor solution in a mould containing the felts, followed by gelation, aging, and drying at 25 ambient pressure.

30

2. The method of Claim 1, wherein drying is achieved with several temperature cycles in the range 60-200°C, over a period between 2 and 9 days.

3. The method of Claim 1, wherein the fibres are felts.

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5 4. The method of Claims 1 and 3, wherein the felts are sewed together to produce panels thicker than those of single felt structures, where the sewing thread is a stranded structure resistant to high temperature.

10 5. The method of Claims 1 to 4, wherein the felts are arranged uniformly and stretched in the mould, ensuring homogeneity and dimensional stability of the panel during the drying stage.

15 6. Aerogel panels obtained with the method described in Claims 1 to 5, wherein:

 a) The panels are folded, wrapped, and unwrapped over themselves, inside or outside the mould, with a radius of curvature down to 2-3 times the thickness of the panel;

20 b) The panels are inserted in a rolling machine and subjected to a compression pressure larger than 1 kPa to be homogenised, cut, trimmed, and subsequently rolled after the compression force is ceased and the panels reach
25 their original thickness;

 c) The panels are subjected to transverse agitation to release the small amount of loose particles present in the panels;

 d) The panels are folded, wrapped, and unwrapped
30 over themselves after immersion in a cryogenic fluid, without losing structural integrity;

 e) The panels are folded, wrapped, and unwrapped over themselves after heating in an oven at least at 350°C, without losing structural integrity.

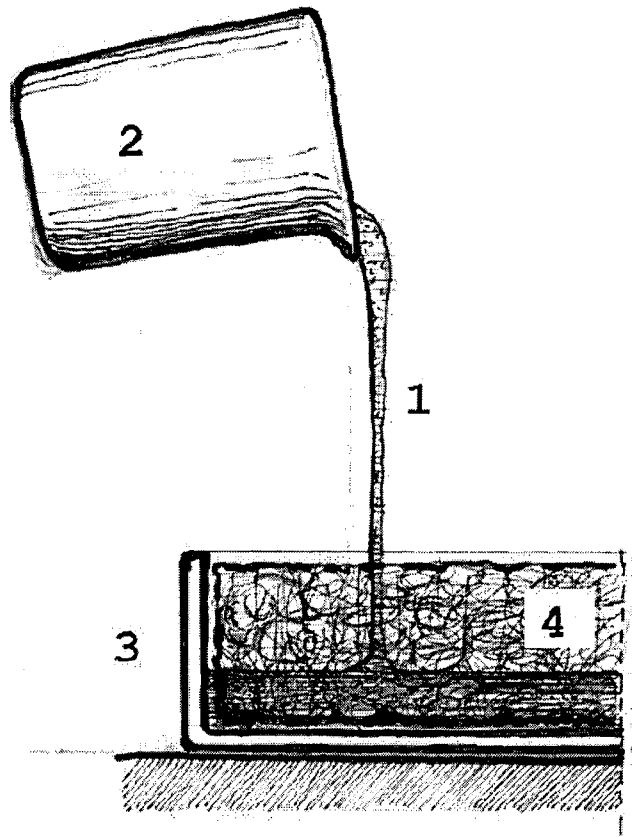


Fig. 1

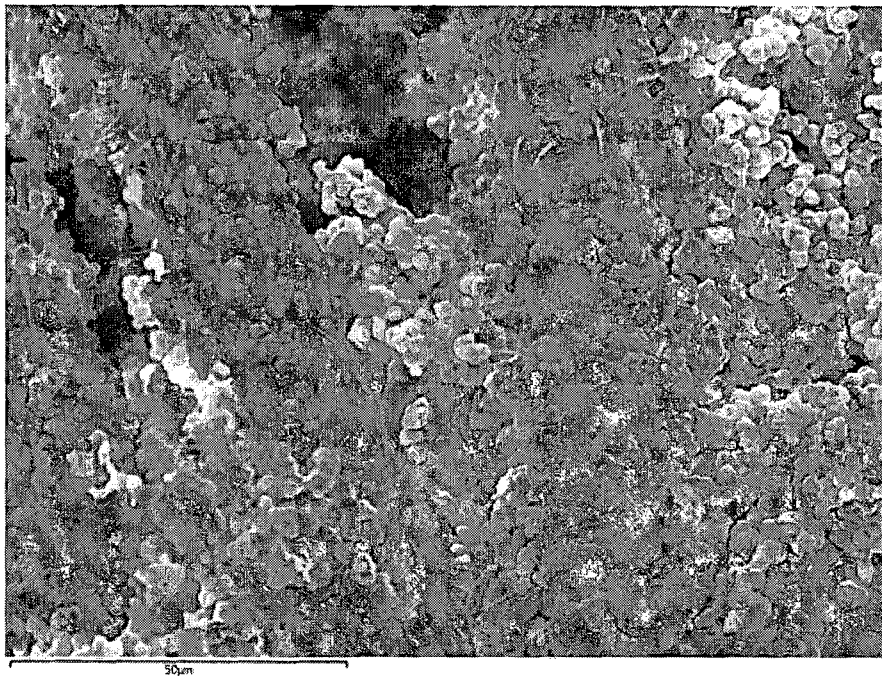


Fig. 2

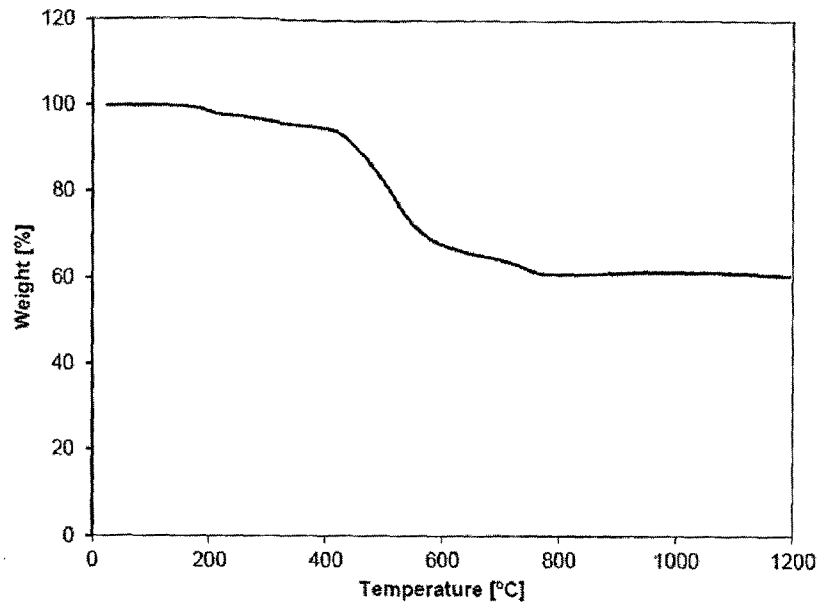


Fig. 3

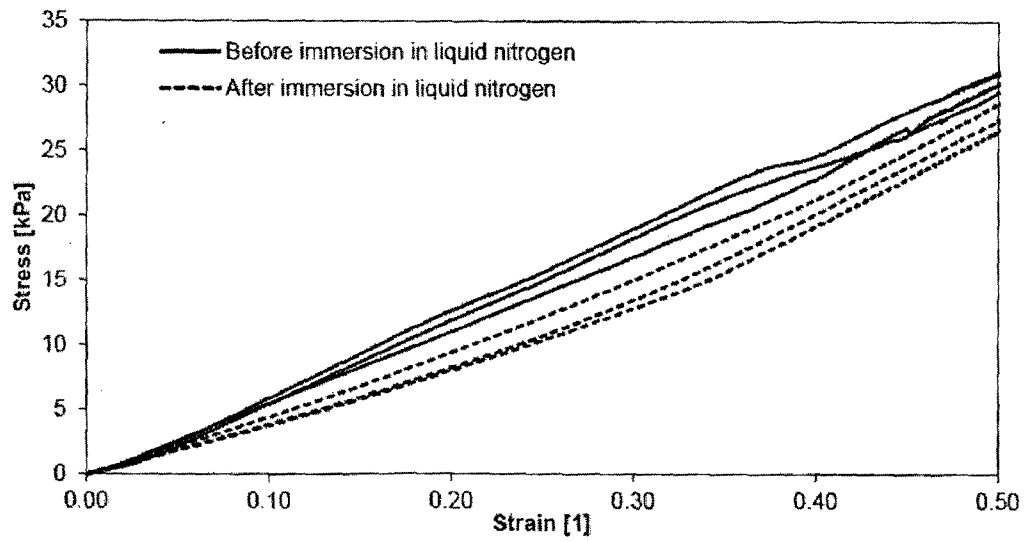


Fig. 4