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(54) Title: AEROGEL AND FOAM FORMATION USING NANOSIZED GAS BUBBLES

(57) Abstract: A method for producing an aerogel and/or foam for manufacturing of paper or paper board, and products thereof, wherein said paper or paper board is manufactured in a papermaking machine, wherein the aerogel and/or foam is formed from gas bubbles having a having a diameter of less than 0.5 micrometer.

AEROGEL AND FOAM FORMATION USING NANOSIZED GAS BUBBLES

Technical field

The present document relates to a method for manufacturing paper and paper board and products made thereof, wherein an aerogel or a foam made from nanosized gas bubbles is used.

Background

In today's paper making process the use of aerogel and foam has become increasingly interesting due to possibilities to make source reduction, water or energy efficient, cost saving and materials with improved or novel features. Foam forming of paper or foam coating of paper, in comparison to conventional wet laid forming, has shown to provide a wide range of products having novel and beneficial characteristics of very even and high porosity structures, for products such as paper, paper board, tissue, hygiene products, insulation materials, composites, filters etc. The use of foam in the paper making process has also opened up for the possibility to use new or traditional raw materials in new ways and in new combinations.

The aerogel or foam can be formed in different ways, conventionally water and air is mixed in presence of foam forming chemicals such as surface active agents e.g. surfactants or tensides, or surface active polymers or particles. The aerogel or foam can also be formed by mechanically mixing fibers and water with foaming agents, such as surfactants or polymers that enables foam generation. In WO2013/160553A1 one such paper or paper board foam forming method is disclosed.

The preparation of smaller foam structures or nanofoam, sometimes also called an aerogel, is usually more challenging. The development of such a nanostructured system is either highly energy demanding or requires a higher content of surface active chemicals.

In liquid packaging board manufacturing the process today is quite complicated and limited to certain chemicals, for example due to safety reasons, costs, and the fact that some chemicals are prohibited for use in food or liquid packaging applications.

When forming a foam or an aerogel, there is often a need to use large quantities of surface active chemicals, which may remain in the paper or board product or cause problems in the process (interfere with other chemicals) or cause weak boundary interfaces causing, for example, reduced fiber-fiber strength or

reduced adhesion to laminated polymer coatings. The surface active chemicals may also have a tendency to migrate and/or to negatively affect the barrier properties. These types of chemicals are often not acceptable to use in the manufacturing of food packaging, or other products, having high demands on the cleanliness of the product. Another drawback of using surface active chemicals such as tensides is that they have hydrophilic part in their structure, which can cause problems in the end product. In certain products there is further a requirement that the product must resist liquid pressure, for instance in hot filling or aseptic sterilization processes with hydrogen peroxide. If there is an external pressure of liquid, the pore size and pore size distribution of the product or substrate becomes critical.

Studies have shown that in foam forming of paper products, the pore size of the substrate is highly dependent on the size of the bubbles in the foam, and that the bubble size of the foam can be affected by several parameters, such as the rotational speed of the mixer, the specific type of surfactant that is used, temperature, electrolyte concentration, pH, co-solvents, and the fibers with which the foam is mixed. When forming paper or board with foam forming techniques instead of using the conventional water forming, it has been shown that the pore size of the paper product is larger (Exceptional pore size distribution in foam-formed fibre networks, Al-Qararah, et al, Nordic Pulp and Paper Research Journal Vol 27, 2/2012, 226-230). There is thus a need for an energy efficient foam forming method of making paper or paper board or products thereof, where the bubble size of the foam, and thus the pore size of the end product including the physical and mechanical properties can be more easily controlled and adjusted.

Summary

It is an object of the present disclosure, to provide an improved method for providing or forming foam in a paper making process.

The object is wholly or partially achieved by a method according to the appended independent claim. Embodiments are set forth in the appended dependent claims and in the following description.

According to a first aspect, there is provided a method for producing an aerogel and/or foam for manufacturing of paper or paper board, and products thereof, wherein said paper or paper board is manufactured on a paper or paperboard machine, wherein the aerogel and/or foam is formed from gas bubbles, wherein a substantial fraction of the gas bubbles have a diameter of less than 0.5 micrometer, and wherein the aerogel and/or foam is formed by introducing said gas bubbles into a liquid suspension.

By aerogel and/or foam is meant that depending on the other process properties, either an aerogel or foam may be produced, or a mixture thereof. This method of forming an aerogel or a foam from gas bubbles being of micro or even nanosize, i.e. so called micro- or nanobubbles, where the aerogel or foam is used in various aspects of paper making in the paper making machine, provides for an aerogel or foam in which the bubble size can be easily controlled and adjusted for the specific application of the aerogel or foam.

The IUPAC definition of an aerogel is a gel which comprised a microporous solid in which the dispersed phase is a gas. However, an aerogel does not have a designated material with set chemical formula but the term is use to group all the material with a certain geometric structure.

The term nanofoam is meant to encompass both the term aerogel and the term foam in the present disclosure, where the aerogel or foam has been produced using nanobubbles of gas.

That the nanobubbles have a diameter of less than 0.5 micrometer is meant that a substantial fraction of the bubbles may be in this size region, but that there may also be larger bubbles present in the gas.

This nanofoam may be produced using conventional means, such as mechanically, by cavitation or using ultrasound or by chemical means, e.g. such chemicals that releases carbon dioxide gas.

The bubble size is also smaller in this nanofoam, than for conventionally formed foams, which further means that the nanofoam is more stable. This means that for some applications of this nanofoam the pore size of the end product can be made much smaller than with conventionally formed foams.

The nanofoam produced by using nanobubbles may further be more stable than conventionally formed foams. By the nanofoam being “stable” is meant that the foam bubbles do not easily collapse. This nanobubble foam may be more easily used in the paper making machine, or may provide that the paper or paper board is more easily processed, e.g. improving runability or dewetting properties of web in the paper making process.

The use of nanobubbles for forming the nanofoam further reduces or even abolishes the need to use foam forming chemicals such as surfactants (tensides) or surface active polymers.

According to one embodiment the aerogel and/or foam may be formed prior to introduction into said papermaking machine.

According to an alternative embodiment said foam may be formed directly in said papermaking machine. The aerogel and/or foam may be formed in a pulper of

the papermaking machine. Alternatively the aerogel and/or foam may be formed in a refiner.

According to one embodiment the foam may be formed prior to introduction into a head-box of the papermaking machine. This means that the nanobubbles may firstly be formed in a separate unit and then mixed with polymers, such as cellulosic fibers or alternatively with a foam. In this way, the problem of creating nanobubbles in a viscous system may be avoided, since this might be difficult to achieve. The nanofoam may for instance be injected into the headbox and then forming a foam-aerogel with other components.

The aerogel and/or foam may, according to one embodiment, be formed directly into a head-box of the papermaking machine. By formed directly in the head-box is meant that aerogel and/or foam is formed in-situ.

The aerogel and/or foam may, according to one alternative embodiment, be introduced as a coating material in the papermaking machine.

The foam may be introduced in a surface sizing step in the paper or board process.

Sizing is used during paper manufacturing to reduce the paper's tendency when dry to absorb liquid. Liquid packaging board and coated fine papers are so called hard sized papers that have the high water resistance. Surface sizing solutions often comprises the use of surface sizing agents such as acrylic co-polymers. In internal sizing the chemicals used at the wet end are often alkyl succinic anhydride (ASA), alkyl ketene dimer (AKD) and rosin. By making the paper web more hydrophobic, the sizing agents influence dewatering and retention of fillers and fibers in the paper sheet.

Further, by introducing the nanobubbles in the sizing step, or wet end, and then drying the paper or paper board a microbubble paper, laminate or paper board may be produced. This material has a very low density, and can be made with existing manufacturing techniques. This paper may thus be a very porous material, for use for instance as a tissue product.

According to one embodiment of the first aspect, wherein said liquid suspension may be any one of water, an aqueous fiber suspension, and an aqueous suspension comprising paper making chemicals or a mixture thereof.

This provides for a method in which the foam may be formed for instance by introducing the nanobubbles into a stream of a fiber suspension, e.g. comprising microfibrillated cellulose, thereby forming a fiber-foam composite which can subsequently be introduced into the paper making machine as a coating of the web.

The foam may further be formed by introducing said gas bubbles into a mixture of water and a surfactant.

According to one embodiment of the first aspect the gas may comprise any one of atmospheric air, pure oxygen, pure nitrogen, pure carbon dioxide, or a mixture thereof.

According to one embodiment the diameter of the gas bubble may be in the range of from 0.01 µm to 0.5 µm, or the diameter of the gas bubbles comprises a mixture of bubbles having different diameters in the range of 0.01 to 0.5 µm.

This means that the bubble size distribution can either be monodisperse, i.e. a large fraction of the bubbles may have the same or substantially the same size, or polydisperse, i.e. the gas bubbles may have different sizes ranging from nanosize to microsize bubbles.

In one embodiment a substantial fraction of the gas bubbles have a diameter which is less than 0.5 micrometers.

According to one embodiment said paper or paper board may be formed from a fibrous material comprising any one of microfibrillated polysaccharide and longer cellulosic fibers, or a mixture thereof. The microfibrillated polysaccharide may for instance be microfibrillated cellulose, cellulose whiskers or microcrystalline cellulose.
According to a second aspect there is provided a method for manufacturing a paper or paper board, formed from a fibrous material comprising any one of microfibrillated cellulose and longer cellulosic fibers, or a mixture thereof, , wherein said method comprises introduction of an aerogel and/or foam produced according to the first aspect, being formed from gas bubbles, wherein a substantial fraction of the gas bubbles have a a diameter of less than 0.5 micrometer, and wherein the aerogel and/or foam is formed by introducing said gas bubbles into a liquid suspension. By "comprises introduction of an aerogel and/or foam" is meant the nanofoam has been introduced in the furnish, in the coating or in the sizing of the paper or paper board.

According to a third aspect there is provided a paper or paper board obtained by the method according to the second aspect.

Detailed description

Foam is conventionally and broadly defined as a colloidal dispersion of gas in a liquid or solid medium. Foam can be generated in many different ways, for instance mechanically, by agitating a liquid medium, optionally with or without surface active agents to promote the foam formation. Foams can also be produced chemically, for instance through fermentation.

An aerogel is conventionally defined a material which is porous and nanostructured, and which has some specific properties such as high porosity and surface area. An aerogel does not have a designated material with set chemical

formula, but the term is use to group all the material with a certain geometric structure.

However, according to this disclosure, the foam, aerogel or nanofoam is produced or formed by using gas bubbles. According to one embodiment an aerogel or a foam is formed from gas bubbles having a diameter of less than 500 nanometers.

The aerogel and/or foam are thus formed from gas bubbles being of micro or even nanosize, i.e. nanobubbles. This means that the foam or aerogel also is nanosized or nanostructured. In the below description the term “nanofoam” is meant to encompass both an aerogel and a foam formed from these nanobubbles of gas.

The nanofoam may also be a material which is a mixture of an aerogel and a foam.

According to one embodiment the gas may be atmospheric air, i.e. a mixture of oxygen, nitrogen and other gases present in the earth’s atmosphere. According to another embodiment the gas is oxygen (O_2). According to another embodiment the gas is nitrogen (N_2). According to yet another embodiment the gas is carbon dioxide (CO_2). According to one embodiment the gas is a mixture of different gases, such as a mixture of air and N_2, or air and CO_2. The gas may also be any other suitable gas or mixture of gases.

According to one embodiment the diameter of the gas or the so called nanobubble or microbubble is in the range of from 0.01 µm to 10 µm. In one embodiment the diameter of the nanobubble is in the range of from 0.01 µm to 1 µm. In another embodiment the diameter of the nanobubble is in the range of from 0.01 µm to 0.8 µm. According to yet an embodiment the diameter of the nanobubble is in the range of from 0.01 µm to 0.6 µm. In one embodiment the diameter is less than 0.5 µm. According to another embodiment the diameter is less than 0.4 µm. According to yet another embodiment the diameter is less than 0.3 µm. According to one embodiment the smallest bubble diameter may be about 0.03 um or in the range of from 0.03 to 0.07 µm.

According to one embodiment there may be a mixture of gas bubbles having different diameters, i.e. a more polydisperse structure including both nanosized and microsized gas bubbles in a mixture, this means that there may be bubbles having a diameter which is more than 0.5 µm. However, the main part or fraction of the gas bubbles used for forming the nanogel are preferably nanosized, i.e. having a diameter of less than 500 nanometers. This means that according to one embodiment the gas bubbles have a monodisperse size distribution.

The nanofoam may be used in the paper or board manufacturing process, for instance as furnish or as additive in a furnish, as a coating or additive in coating or at or in a sizing step in the process. The paper or board manufacturing process thus encompasses both so called foam forming processes and more conventional processes such as wet laid paper processes or air laid paper processes.

The nanofoam itself may be formed in different ways using the gas nanobubbles.

According to one embodiment the nanobubbles of gas may be introduced into a liquid suspension.

The liquid suspension may be an aqueous suspension comprising for instance different types of fibrous materials, and/or different types of chemicals, such as foam forming chemicals, paper making additives (fillers etc), sizing chemicals and so on.

The nanofoam may for instance be formed by introducing the nanobubbles of gas into a cellulose gel or suspension comprising microfibrillated cellulose (MFC). It can be a mixture of highly refined fibers (MFC), nanocellulose or cellulose nanocrystals (CNC), microcrystalline cellulose and traditional or conventional pulp fibers, or mixtures thereof.

According to one alternative embodiment synthetic fibers may be included in the liquid suspension, such as e.g. polylactic acid (PLA), or polyvinyl alcohol (PVA) or polyethylene terephthalate (PET) fibers.

According to one embodiment the nanofoam may be produced prior to introducing it into the paper or board manufacturing process. This may be useful in applications such as when the nanofoam is used for coating of a wet laid paper web, or when the foam is used in a sizing step in the paper or board manufacturing process.

According to one embodiment the nanofoam may be used as a furnish, i.e. in the paper making pulp solution prior to its introduction into a papermaking machine, i.e. for instance in the pulper or refiner. This means that the nanofoam itself may be used to form the paper or paper board end product.

Through this alternative embodiment, products having a very high porosity may be obtained, for instance papers for tissue applications.

The nanofoam may also, according to another embodiment, be added into the paper making process at different stages.

According to one alternative embodiment the nanobubbles of gas may be introduced directly into the papermaking machine, such as in the cleaner, the head-

box or in a sizing step, thus forming the nanofoam in-situ in the papermaking machine.

The nanofoam may also be used as a coating and applied in the paper or board manufacturing process at any coating step or stage. The nanofoam may alternatively be mixed with other coating additives and chemicals.

According to one embodiment the nanofoam may be supplied to the papermaking machine in a continuous manner. According to one embodiment the nanofoam may be fed into the head-box, to be mixed with the water and fiber mixture, before forming the web in the wire section.

According to one embodiment the nanofoam may be fed onto the wire section together with the fiber and water mixture from the head-box.

According to one embodiment the nanofoam may be used in a sizing step in the paper or board manufacturing process. By using a nanofoam it may be possible to reduce the or even completely abolish the use of these different types of internal and surface sizing agents.

Further, by introducing the nanobubbles in the sizing step, or wet end, and then drying the paper or paper board a microbubble paper, laminate or paper board may be produced. This material has a very low density, and can be made with existing manufacturing techniques. This paper may thus be a very porous material, for use for instance as a tissue product.

According to one embodiment, the end product, when using the nanofoam in the process, may be a thermoplastic product.

According to another embodiment the end product may be ply paper or an application of a ply paper, e.g. in a board application.

According to another embodiment the nanofoam may be used for paperboard applications.

Other possible applications may include producing intermediate composites which can be used in different types of subsequent applications in the paper or board making process.

In view of the above detailed description of the present invention, other modifications and variations will become apparent to those skilled in the art. However, it should be apparent that such other modifications and variations may be effected without departing from the spirit and scope of the invention.

CLAIMS

1. A method for producing an aerogel and/or foam for manufacturing of paper or paper board, and products thereof, wherein said paper or paper board is manufactured in a papermaking machine,
c h a r a c t e r i z e d in that
the aerogel and/or foam is formed from gas bubbles, wherein a substantial fraction of the gas bubbles have a diameter of less than 0.5 micrometer, and wherein the aerogel and/or foam is formed by introducing said gas bubbles into a liquid suspension.

2. The method as claimed in claim 1, wherein said aerogel and/or foam is formed prior to introduction into said papermaking machine.

3. The method as claimed in claim 1, wherein said aerogel and/or foam is formed directly in said papermaking machine.

4. The method as claimed in claim 3, wherein the aerogel and/or foam is formed in a pulper or refiner of the papermaking machine.

5. The method as claimed in claim 2, wherein the aerogel and/or foam is formed prior to introduction into a head-box of the papermaking machine.

6. The method as claimed in claim 3, wherein the aerogel and/or foam is formed directly into a head-box of the papermaking machine.

7. The method as claimed in claim 2, wherein the aerogel and/or foam is introduced as a coating material in the papermaking machine.

8. The method as claimed in claim 2, wherein the aerogel and/or foam is introduced in a sizing step in the paper or board process.

9. The method as claimed in claim 2, wherein said liquid suspension is any one of water, an aqueous fiber suspension, and an aqueous suspension comprising paper making chemicals or a mixture thereof.

10. The method as claimed in claim 9, wherein the foam is further formed by introducing said gas bubbles into a mixture of water and a surfactant.

11. The method as claimed in any one of the preceding claims, wherein the gas comprises any one of atmospheric air, pure oxygen, pure nitrogen, pure carbon dioxide, or a mixture thereof.

12. The method as claimed in any one of the preceding claims, wherein the diameter of the gas bubble is in the range of from 0.01 μm to 0.5 μm, or the diameter of the gas bubbles comprises a mixture of bubbles having different diameters in the range of 0.01 to 0.5 μm.

13. The method as claimed in any one of the preceding claims, wherein said paper or paper board is formed from a fibrous material comprising any one of microfibrillated cellulose and longer cellulosic fibers, or a mixture thereof.

14. A method for manufacturing a paper or paper board, formed from a fibrous material comprising any one of microfibrillated cellulose and longer cellulosic fibers, or a mixture thereof, wherein said method comprises introduction of an aerogel and/or foam produced according to any one of claims 1 to 13, being formed from gas bubbles, wherein a substantial fraction of the gas bubbles have a a diameter of less than 0.5 micrometer, and wherein the aerogel and/or foam is formed by introducing said gas bubbles into a liquid suspension.

15. A paper or paper board obtained by the method as claimed in claim14.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H21/56 B01F17/00 D21F11/00 C08J9/30
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)
D21H B01F D21F C08J

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	JP 2003 192991 A (OJI PAPER CO) 9 July 2003 (2003-07-09) the whole document	1-15
X	WO 2005/030847 A1 (VALTION TEKNILLINEN [FI]; JOHANSSON ALLAN [FI]; QVINTUS-LEINO PIA [FI]) 7 April 2005 (2005-04-07) sentence 28, paragraph 6 - sentence 19, paragraph 7	1,2,7, 11,15
X	WO 2009/106968 A2 (STORA ENSO OYJ [FI]; BACKFOLK KAJ [FI]; HEISKANEN ISTO [FI]; HARLIN AL) 3 September 2009 (2009-09-03)	1,2,15
A	page 7, last paragraph - page 8, last paragraph; claims	3-14

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

Information on patent family members

International application No
PCT/IB2016/052895

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