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(71) Applicant: Center of Excellence Polymer Materials and Technologies (Polimat)  
1000 Ljubljana (SI)

(72) Inventors:

- Mozetic, Miran  
1000 Ljubljana (SI)
- Vesel, Alenka  
8210 Trebnje (SI)

- Stana-Kleinschek, Karin  
2000 Maribor (SI)
- Persin, Zdenka  
2000 Maribor (SI)

(74) Representative: Schmidt, Karsten et al  
ZACCO GmbH  
Bayerstrasse 83  
80335 München (DE)

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### (54) Method for increasing the hydrophilicity of polymeric materials

(57) A method for increasing the hydrophilicity of a fibrous or porous polymeric material in a sample comprising

prising said polymeric material, comprises contacting said sample with an oxidizing gas comprising an oxidizing component.

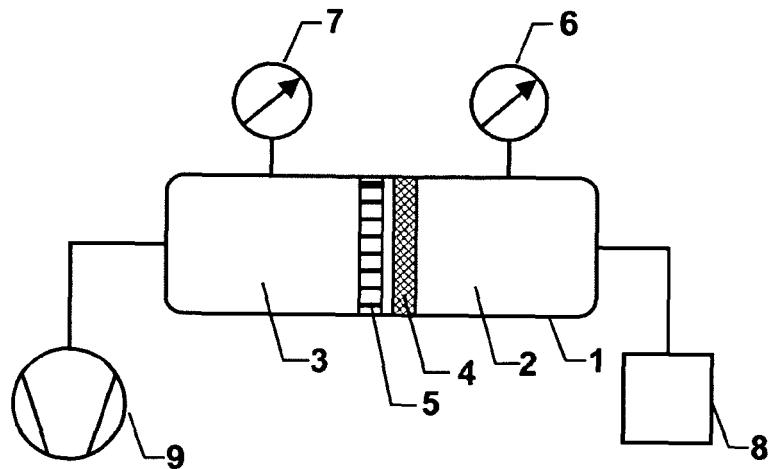


Figure 1

**Description****FIELD OF THE INVENTION**

**[0001]** The present invention relates to methods of increasing the hydrophilicity of porous or fibrous polymeric materials, as well as materials and products produced thereby.

**BACKGROUND OF THE INVENTION**

**[0002]** Porous or fibrous polymeric materials are used as absorbent material in numerous industrial products, such as, e.g., absorbent products, diapers, incontinence products, wound dressings and the like. They also find application in the garment products, in particular functional sportswear, and footwear. In such products, a high degree of hydrophilicity is desired, because a strongly hydrophilic material will result in a faster and more complete uptake of aqueous liquids into the material. Various methods of increasing the hydrophilicity of polymeric materials have been described to date.

**[0003]** To improve the hydrophilicity of textile materials (i.e. fibers, yarn, fabric, non-wovens) chemical processes have been used. The use of enzymes to improve the hydrophilicity of textile materials is described in the US2010047533 (oxidoreductase) and the US2003119172 (pectinase, cellulase, protease, and lipase).

**[0004]** JP10088478 describes the improved hydrophilicity of cellulose fiber on the basis of its wetting in non-ionic tenside.

**[0005]** In addition to a softer feel, the use of softening agents (WO03060051, EP1116813, DE10034232, and US5277968) also improves the hydrophilicity of textile materials. However, such chemical processes may be hazardous for the environment and they degrade the mechanical-technological properties of treated materials.

**[0006]** The use of thermodynamically unstable physical technologies using gas plasma is an environmentally-friendly alternative. Depending on the type and nature of the gas used various surface modifications can be achieved. The use of oxygen plasma to improve the hydrophilicity of non-cellulosic membranes and films is described in the JP2009126758, JP2003342400, JP2208333 and JP59089758.

**[0007]** The use of corona plasma to improve the hydrophilicity of resins is described in the JP2000143850 and JP2000109580. Atmospheric plasma has been shown to be an effective activation technique for resin surfaces and the surfaces of materials in powder or particle form (KR20020090583, JP9141087 and JP6134296).

**[0008]** With the use of iodine plasma (JP6228344) the hydrophilic-hydrophobic balance on the surface of polymeric materials was successfully adjusted.

**[0009]** EP0127149 describes the use of vacuum plasma to improve the adhesion of polyolefin films.

**[0010]** US2010028572 describes the industrial use of water vapour plasma to improve the hydrophilicity of electronic components (metal, ceramic, fluorocarbon and polyamide resins).

**[0011]** The plasma-based ion deposition technique (NaCl or MgCl<sub>2</sub> solution) with the purpose of improving the wetting of the implant's surface is described in the GB2468198.

**[0012]** Cold plasma using polar gases causes the incorporation of hydroxyl, amino, imido, carboxyl etc. radicals onto the surface of the polymer and consequently lowers the water contact angle, i.e. improves hydrophilicity (CN1858334).

**[0013]** Plasma using an O<sub>2</sub> and N<sub>2</sub> gas mixture ensured the long-term hydrophilicity of the surface of fuel cells with bipolar plates (US2006263670) and improved the adhesion of the protective metal coating in electrical installations (EP1312696).

**[0014]** Treatment with corona plasma and/or plasma based on a mixture of fluorine and oxygen led to the incorporation of hydrophilic functional groups onto the surface of various resins (polyolefin, polyester, polyacetal etc.), which consequently reduced the contact angle to 40° (JP2001019857).

**[0015]** Plasma from a mixture of inert gases and oxygen was used to improve or to ensure the long-term hydrophilicity of samples made of plastic (JP8176327).

**[0016]** Plasma based on an O<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, N<sub>2</sub>O, CO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub> gas mixture was used as a pre-treatment to improve the hydrophilicity of materials in powder or granule form in the final production process of thermoplastic products (DE4141805).

**[0017]** In order to significantly improve hydrophilicity and adhesion, whilst having a minimal effect on the roughness, the surface of a polymer containing fluorine-containing functional groups was treated with atmospheric plasma using a mixture of fluoride-carbon gases, oxygen gas or gas containing oxygen and gas containing nitrogen functional groups (JP3290442).

**[0018]** In order to improve the hydrophilicity of polyethylene terephthalate, polycarbonate and cellulose acetate, a surface plasma treatment based on using an A, He, H<sub>2</sub>, Kr, Ne, N<sub>2</sub>, Xe gas mixture (GB1215234) was used.

**[0019]** An overview of the patents in the field of textile materials includes the use of plasma with non-polymerized gases to improve the hydrophilicity and moisture absorption of woven products (CN101113567); plasma with a mixture of carbon, hydrogen, silicon, nitrogen, sulphur and oxygen gases to improve the hydrophilicity of woven products, non-woven products, garments etc. not only on the surface but also in the pore interior (US2005181198); cold plasma to improve the hydrophilicity and durability of the color tone of the fibers (JP1239179); cold plasma with gas containing nitrogen (N<sub>2</sub>, NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>), oxygen (O<sub>2</sub>, CO<sub>2</sub>), or sulphur (SO<sub>2</sub>, H<sub>2</sub>S) groups to achieve stability in the hydrophilic properties of yarn on the exterior as well as on the interior

surface and in its pores (JP61086908).

[0020] By using graft polymerisation good wetting of various materials, such as the combustible cell separator (US2009098431), fluoride resin (US2003008935), and polyolephine foam (JP63223046) can also be achieved.

[0021] By polymerising ethylene oxide on the surface of cellulose, improved hydrophilicity of paper was achieved (JP2005042238).

[0022] Treatment with ionising radiation to increase hydrophilic properties is also effective for porous materials (non-wovens, knitted products, membranes) (JP11012376, JP7138391, and JP1030606).

[0023] Surface treatment using plasma polymerisation with helium gas and subsequent post-treatment using plasma containing hydrogen, oxygen, nitrogen and argon gases significantly improve the hydrophilicity of the treated material (KR20020086139).

[0024] Surface treatment with the formation of coating/layers on the surface of materials is one of the treatments used to improve hydrophilicity. KR20080001444 describes the procedure of forming an oxygen coating on the surface of a superconductor, and the TW276476 describes the formation of an inorganic coating on glass, porcelain and graphite.

[0025] The production of a hydrophilic film on the surface of medical polyurethane material and its advantages are described in CN101386684.

[0026] The production of an ultra-hydrophilic thin Ti-O-C film on the surface of a metal material results in extreme hydrophilicity and material stability, which consequently leads to more efficient production and rationalised costs (KR20070026496).

[0027] TW588432 describes the manufacture of isolators using the plasma modification process, which results in Si-N, Si-O and Si-H coatings on surfaces that improve the hydrophilicity of the material.

[0028] The simplest production method of an Al layer on the surface of a material that can subsequently show water-repellent and hydrophilic properties is described in the JP2002138156.

[0029] A thin film i.e. a polyamine layer that can be applied to any surface results in extreme hydrophilicity and anti-dew properties of the material (JP2070768).

[0030] Permanent hydrophilicity of objective glass is ensured by the formation of a surface layer containing nitrogen functional groups (JP62260836).

[0031] In order to improve hydrophilicity a combination of chemical and physical material surface treatments can also be used. JP3254752 describes the use of such a combination for the surface treatment of a hydrophobic material (artificial vein).

[0032] GB2430201 describes a combination of both techniques on a thin layer of a transistor or diode by using plasma to achieve an etching effect followed by chemical treatment with fluoroalkyl silanizing agents. Thereby the difference between hydrophilic or oil-repellent properties is clearly shown on the material's surface.

[0033] The MX01011851 describes the modification of

a contact lens surface to improve hydrophilicity by creating a carbon surface layer followed by plasma oxidation and plasma polymerisation.

[0034] The production of a thin film to improve hydrophilicity includes a chemical treatment with organic solvents, acidic and alkaline treatments and a physical treatment using the so-called "after glow discharge" plasma (JP2001049444).

[0035] The activation of aliphatic polyester surfaces for improved bio-compatibility or bio-absorbency, as described in the US6107453, is performed in the following phases: acidic or alkaline hydrolysis, cold plasma treatment, chemical reactions or electromagnetic radiation.

[0036] Corona or oxygen plasma were used to activate the synthetic polymer and produce a cross-linked polysaccharide layer on the surface and thereby improve the hydrophilicity, mechanical properties and resistance to chemicals (JP63301234).

[0037] The JP59215328 describes the process of achieving a permanent hydrophilicity effect by creating a surface methacrylate layer that is polymerised into a thin film when using plasma and shows a hydrophilic effect upon subsequent water vapour treatment. The process of treating silicone resin to achieve a permanent hydrophilic effect is described in the JP56000831, where the product was first exposed to plasma containing inorganic gases, and subsequently treated with a solution of surfactants.

[0038] JP9143884 is well-known in the field of textile materials; it describes a combination of chemical and physical treatments of a synthetic garment, namely crosslinking with polysiloxane derivatives, followed by treatment with oxygen plasma to achieve hydrophilicity and resistance to melting.

[0039] Despite the various methods known for increasing hydrophilicity of polymeric materials described above, there remains a need for improved methods of increasing the hydrophilicity of polymeric materials, which overcome common disadvantages of the presently known methods. For example, the above described chemical processes used to improve the hydrophilicity of textile materials (e.g., fibers, yarns, woven and non-woven products) are hazardous to the environment, or deteriorate the mechanical properties of the treated materials. Methods using thermodynamically unstable chemical matter, e.g. plasma, are environmentally friendly, but they increase the hydrophilicity of a sample of the material only at its outer surface. The core of sample material will remain un-affected.

## SUMMARY OF THE INVENTION

[0040] Against the background the present invention addresses the need for further and improved methods of increasing the hydrophilicity of polymeric materials. In particular, the present methods do not only increase the hydrophilicity of a sample at its outer surface, but also fibers and pores in the interior of the sample will be af-

fected.

**[0041]** The present invention is defined by the appended claims. Hence, it provides a method for increasing the hydrophilicity and/or wettability of a sample comprising porous or fibrous polymeric materials by contacting the sample with an oxidizing gas comprising an oxidizing component, such as, e.g., a gas comprising atomic oxygen. The present invention also relates to materials produced (i.e., modified) by methods of the present invention, and to products produced from such materials.

**[0042]** The present invention hence relates to a method for increasing the hydrophilicity of a polymeric material in a sample comprising said material, said method comprising contacting said sample with an oxidizing gas comprising an oxidizing component.

**[0043]** Accordingly, the present invention also relates to methods for increasing the wettability of a polymeric material by measures described in this application.

**[0044]** In a preferred embodiment, said oxidizing component is atomic oxygen.

**[0045]** In a further preferred embodiment, said polymeric material is selected from the group consisting of biopolymers, synthetic polymers, cellulose, starch, protein, polyethylene, polypropylene, polyurethane, polyterpene, inorganic polymers, phenolic resins, polyanhydrides, polyester, polyolefins, polyalkenes, polyamide, polyacetal, polyethylene terephthalate, polycarbonate, and cellulose acetate.

**[0046]** A particularly preferred polymeric material is cellulose.

**[0047]** In preferred embodiments of the invention, the polymeric material is a porous or fibrous material.

**[0048]** When porous or fibrous materials are used, the method preferably comprises perfusing said sample with said oxidizing gas. In this case, a pressure difference is preferably established between two opposing sides of said sample.

**[0049]** In preferred embodiments of the invention, the porous or fibrous polymeric material is a woven material, a non-woven material, a knitted material, a crocheted material, a spun-bonded material, melt-blown material, a foamed material, or a sintered material.

**[0050]** In preferred embodiments, the flux of the oxidizing component, e.g., atomic oxygen, into the sample is between  $10^{20}$  atoms/m<sup>2</sup>/s and  $10^{23}$  atoms/m<sup>2</sup>/s.

**[0051]** In further preferred embodiments, the ratio between the flux of the oxidizing component out of the sample [atoms/m<sup>2</sup>/s] and the flux of the oxidizing component into the sample [atoms/m<sup>2</sup>/s] is between 0.01 and 0.999, preferably between 0.1 and 0.9, most preferred between 0.3 and 0.7. The ratio can thereby be adjusted to obtain the homogenous modification of the material throughout the entire sample, while at the same time ensuring efficient use of the oxidizing component.

**[0052]** Preferably, the contacting is at a maximum temperature of between 20°C and 300°C, preferably between 20°C and 150°C, most preferred between 20° and 80°C. This is to ensure that no uncontrolled oxidation

occurs, which may negatively affect the material's properties.

**[0053]** In methods of the invention, the contacting step is preferably in a dry state.

**[0054]** The present invention also relates to polymeric material modified by a method of any one of claims 1 to 11. Such material has advantageous properties, in particular, significantly increased hydrophilicity. Preferably, the modified material of the invention is a porous or fibrous material.

**[0055]** The present invention also relates to a product comprising the polymeric material of the invention. In preferred embodiments, the product is selected from the group of products consisting of diapers, incontinence products, wound dressings, medical patches, hygienic pads, feminine hygiene articles, sanitary towels, garment products, footwear products, sintered products, membranes, filters, implantable medical products.

## 20 BRIEF DESCRIPTION OF THE DRAWINGS

### [0056]

25 Figure 1 shows an arrangement useful for conducting a method of the invention.

Figure 2 visualizes the depletion of the oxidizing component in oxidizing gas upon passing through a sample of polymeric material in a method according to the invention. Shown is the ratio of the atomic oxygen flux out of a sample according to the invention [atoms/m<sup>2</sup>/s] and the atomic oxygen flux into the sample [atoms/m<sup>2</sup>/s] versus the atomic oxygen flux into the sample [ $10^{23}$  atoms/m<sup>2</sup>/s].

30 Figure 3 shows experimental results obtained from treated and non-treated polymeric materials according to the invention.

## DETAILED DESCRIPTION OF THE INVENTION

40 **[0057]** The expression "hydrophilicity", according to the present invention, shall be understood to define the tendency of a material to be wetted by aqueous liquids. Accordingly, the hydrophilicity of a polymeric material is the tendency of water to adhere to or spread over the

45 material's surface. In accordance with one aspect of the invention, the expression hydrophilicity can be equated with "wettability". The increase of the hydrophilicity of a sample of porous or fibrous polymeric material can manifest itself in an increased capillary velocity (i.e., the initial slope of the  $m^2 = f(t)$  absorption curve, see Figure 3).

50 **[0058]** Hence, in accordance with one aspect, of the invention, "increasing the hydrophilicity" of a sample shall be understood as meaning an increase in the capillary velocity of a sample, measured by the method of Example 2, by at least 10%, preferably at least 50%, or at least 100%, or at least 500%, most preferably at least 1000%.

**[0059]** In another preferred embodiment of the invention, the increased hydrophilicity of a sample of polymeric

material manifests itself in an decreased average contact angle determined by the Powder Contact Angle method described in Persin Z, Stana-Kleinschek K, Sfiligoj-Smole M, Kreze T and Ribitsch V. Determining the surface free energy of cellulose materials with the powder contact angle method. *Textil Res J* 2004; 74: 55-62. Preferably, the average contact angle is reduced by at least 10%, or by 20%, or by at least 40%, according to the above method.

**[0060]** An "oxidizing gas", according to the invention, shall be understood as being a gas, comprising at least one oxidizing component, said gas being capable of oxidizing polymeric materials. Preferably, the oxidizing gas is capable of oxidizing the polymeric materials of the invention at a temperature below 300°C, even more preferred, below 80°C. The oxidizing gas may comprise at least one oxidizing component, e.g., atomic oxygen, or ozone, as well as non-oxidizing components, such as air, nitrogen gas, molecular oxygen (O<sub>2</sub>) and/or carbon dioxide.

**[0061]** In one preferred embodiment, the oxidizing component is electronically excited oxygen molecule. Electronically excited oxygen molecule shall be understood to be oxygen molecule having electrons in an excited energy state, excited by at least 1 eV (per oxygen atom).

**[0062]** "Atomic oxygen", according to the invention, shall be understood to relate to a single oxygen atom (O<sub>1</sub>) not covalently bound, or connected to, a further atom. In preferred embodiments, the atomic oxygen is in free radical form. Atomic oxygen, according to the invention, is preferably not electrically charged. Hence, oxygen plasma is excluded.

**[0063]** "Perfusing" a sample of porous or fibrous material, according to the present invention, shall be understood as relating to the act of establishing forced migration of a gas through a sample of the porous or fibrous material. Preferably, perfusion of the sample with gas is effected by establishing a pressure gradient within (or across) said sample. Perfusion is thus the passing through of gas through the porous or fibrous material.

**[0064]** "Cellulose", according to the invention, shall be understood to be the organic compound with the formula (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>, a polysaccharide comprising a linear chain of  $\beta$  (1→4) linked D-glucose units.

**[0065]** The method according to the invention encompasses a treatment for the interior of porous material using gas atoms and molecules that cause oxidation of the organic material through a procedure conducted in an apparatus shown schematically in Figure 1. The apparatus includes a chamber 1 having two compartments: A high-pressure compartment 2 and a low-pressure compartment 3. The sample 4 of a porous or fibrous material is placed in between the two compartments 2, 3 of the chamber 1. The sample is preferably supported by a support 5, such as a firm mesh, a frit, or sintered material, which enables the sample 4 to maintain its shape despite a substantial pressure difference between its opposing

surfaces facing the high-pressure compartment 2 and the low-pressure compartment 3. A pressure difference is generated by pressure generating means 9, e.g., a pump. The arrangement shown in Figure 1 includes a source 8 of oxidizing gas, providing a continuous stream of oxidizing gas comprising a preferably constant amount of an oxidizing component, in this case, atomic oxygen.

**[0066]** Various methods of generating atomic oxygen are known in the art. For example, atomic oxygen can be generated by heating oxygen molecules to temperatures above 1000°C, and allowing surface dissociation of oxygen molecules on selected catalytic materials (usually platinum). Alternatively, atomic oxygen can be produced, e.g., by passing pure oxygen gas (O<sub>2</sub>) through a glass tube having external electric coils connected to a radio frequency generator. The radio frequency generator suitably operates at P = 50 W and produces, through the coils, a radiofrequency field of between 1 MHz-100 MHz, preferably 27 MHz. Optionally, the gas is heated to a temperature of e.g. 1000°C prior to entering the radio frequency field.

**[0067]** A suitable concentration of atomic oxygen in the oxidizing gas is 1%-100%, preferably 1-50%, more preferred 1-20%, most preferred 10% (mol/mol).

**[0068]** The oxidizing component of the oxidizing gas enables oxidation of the polymeric material (e.g. polymeric organic material) at a temperature significantly lower than that needed for thermal degradation/pyrolysis of the polymeric material. The concentration of the oxidizing component in the oxidizing gas in each of the high-pressure compartment 2 and the low-pressure compartment 3 is approximately constant / homogeneous. The oxidizing component first contacts the polymeric material of sample 4 at the side of the sample facing the high-pressure compartment 2. The atoms or molecules of the oxidizing component do not adhere on or bounce off the surface of the sample 4, but they penetrate or pass through the sample 4, due to the pressure gradient produced by the difference in pressure between the high-pressure compartment 2 and the low-pressure compartment 3. Gas meters 6, 7 for metering the concentration of the oxidizing component in the oxidizing gas are arranged in the high-pressure compartment 2 and in the low-pressure compartment 3, respectively. The gas meter arranged in the high-pressure compartment 6 measures the concentration of the oxidizing component in the high-pressure compartment 2, and the gas meter arranged in the low-pressure compartment 7 measures the concentration of the oxidizing component in the low-pressure compartment 3. Since the concentration of the oxidizing component in both compartments of the chamber 1 is approximately constant and homogeneous, the difference in concentration of the oxidizing component detected by the meters 6, 7 is a measure of the oxidizing component lost due to the reaction with the material in sample 4. If the loss is high, the meter 7 shows a value significantly lower than the value shown by the meter 6. If the loss is very low, the meter 7 shows substantially

the same value as meter 6.

**[0069]** Very high loss results in non-uniform treatment of the sample 4. The part of the sample 4 closer the high-pressure compartment 2 is treated more efficiently than parts of sample 4 closer the low-pressure compartment 3. Hence, a too high loss of oxidizing component in the oxidizing gas upon passing through sample 4 is undesirable.

**[0070]** A low loss of oxidizing component results in a balanced treatment of all parts of sample 4. This is desirable. However, an unfavorable effect is the poor yield (inefficient use) of the reactive atoms/molecules in the oxidizing component. Optimal conditions, in the sense of satisfactory uniformity and a good yield of atoms and molecules, are achieved when approximately 3% to 70% of the oxidizing component is lost due to the oxidation reaction.

**[0071]** The reaction between the oxidizing component and the polymeric material of sample 4 is exothermic and results in heating of the sample 4. To a certain degree, such heating is desirable, since it intensifies the interaction and promotes oxidation. However, a high temperature is not desired, since it can also lead to uncontrolled oxidation (pyrolysis) and thereby change the properties of the material to the worse. The concentration of the oxidizing component in the high-pressure compartment 2, therefore, has to be adjusted to the specific properties of the sample 4.

**[0072]** Treating a sample of a polymeric material with an oxidizing gas by methods according to the invention leads to greatly improved hydrophilicity and/or wettability of the sample of porous or fibrous material not only at the sample's outer surface, but throughout the entire sample. Thereby, a very homogenous and complete modification of the material's properties, in particular hydrophilicity and wettability, is achieved.

**[0073]** Figure 2 shows the depletion of the oxidizing component (in this case, atomic oxygen) in the oxidizing gas, upon forced migration through a sample of cellulose. Shown is the ratio between the flux of the oxidizing component flowing out of the sample (at the side facing the low-pressure compartment 3; [atoms/m<sup>2</sup>/s]) relative to the flux of the oxidizing component into the sample (at the side facing the high-pressure compartment 2; [atoms/m<sup>2</sup>/s]), as a function of the flux of the oxidizing component into the sample (at the side facing the low-pressure part 3; [10<sup>23</sup> atoms/m<sup>2</sup>/s]). As can be seen, the depletion of oxidizing component is around 50%, which provides efficient use of the oxidizing component (in this case, atomic oxygen) in the oxidizing gas, but also provides sufficiently uniform treatment of the polymeric material.

#### EXAMPLE 1

**[0074]** The hydrophilicity of polysaccharide sample treated in accordance with a method of the present invention is measured. Hydrophilicity is assessed in terms

of the time required for a liquid to be taken up by treated and non-treated samples of polymeric materials, respectively. In this experiment, the polymeric material is cellulose. The oxidizing component is atomic oxygen.

**[0075]** The results of the measurement are presented in Figure 3. The capillary velocities of non-treated porous material are compared to the same material treated by methods of the invention. The treatment of the material was performed in an apparatus as shown in Figure 1. The flux of the oxidizing component, in this case atomic oxygen, at the side facing the high-pressure compartment 2 of chamber 1, was 2.5 x 10<sup>23</sup> atoms/m<sup>2</sup>/s.

**[0076]** Capillary velocities were monitored using a modified Powder Contact Angle method developed for determining the hydrophilic/hydrophobic properties of porous materials. The monitoring was performed as follows: A porous sample, composed of cellulose material, was cut into 2 x 5 cm rectangular pieces and suspended in a special sample holder apparatus. A vessel was filled with a wetting liquid (water) and was placed in the apparatus on a driving table. When the apparatus was turned on, the liquid-filled vessel started slowly moving upwards. As soon as the sample edge contacted the liquid surface, the absorption was monitored. The weight-gain m [g] of the sample, during liquid absorption, was monitored as a function of time t [s]. The square of the weight gain, m<sup>2</sup>, is plotted over time. The initial slope of the function m<sup>2</sup> = f(t) is known as the capillary velocity, which characterizes the rate of water absorption.

**[0077]** For both, treated and non-treated sample, Figure 3 shows the squared adsorbed mass versus time. At the beginning of the absorption, the slope is steep, while after a certain period of time the curve reaches a plateau, indicating that complete wetting occurred. The results in Figure 3 indicate that the imbibition of water was significantly slower for the non-treated sample, as compared to the treated sample. Even after 100 s, the non-treated sample was not completely wetted (i.e. a plateau was not yet reached). Within 100 s, the non-treated sample absorbed approx. 1.06 g of water. Significantly faster capillary velocity was observed in the cellulose sample treated according to the invention. The capillary velocity (initial slope of the m<sup>2</sup> = f(t) curve) of the treated sample was approximately 40 times higher (4000%) than with the non-treated sample. This proves a dramatic increase in the hydrophilicity of the sample. As shown in Figure 3, the curve for the treated cellulose sample reached a plateau within 20 s, where after the mass of the sample remained substantially unchanged (no further uptake of water was evidenced). Within 20 s, the treated sample was able to absorb approx. 1.2 g of water, which is significantly more than observed for the non-treated sample (which corresponds to a 13% increase).

**[0078]** Thus, the treatment procedure resulted in a significant increase in the absorption velocity and absorption capacity.

**[0079]** Without wishing to be bound by theory, it is believed that during the treatment procedure, the formation

of new functional groups (aldehyde, ketone and carboxyl) at the cellulose surface has occurred. Furthermore, not only formation of new reactive functional groups at the sample surface, but also activation of hydroxyl groups already present in the cellulose sample may have a positive effect on the hydrophilicity of the polymeric material.

#### EXAMPLE 2 - DETERMINATION OF CAPILLARY VELOCITY

**[0080]** A porous or fibrous sample is cut into a disc-shape having a diameter of 2.5 cm and a thickness of 0.3 cm. The disc is disposed in an upright (vertical) orientation above a water surface (de-ionized water, preferably equal to or greater than 100 cm<sup>2</sup>), and brought into contact with said liquid surface at its lower peripheral edge, whereupon the weight gain m [g] is measured over time. The capillary velocity is determined as the initial slope (dm<sup>2</sup>/dt [g<sup>2</sup>/s], linear part) of the squared mass over time (m<sup>2</sup> = f(t)) curve. The temperature is 20°C.

**[0081]** An increase of the capillary velocity is determined as the percent increase of the capillary velocity of a treated sample over a non-treated (but otherwise identical) second sample.

#### EXAMPLE 3 - DETERMINATION OF THE ABSORPTION CAPACITY

**[0082]** A porous or fibrous sample is cut into a disc-shape having a diameter of 2.5 cm and a thickness of 0.3 cm. The disc is disposed in an upright (vertical) orientation above a water surface (de-ionized water, preferably equal to or greater than 100 cm<sup>2</sup>), and brought into contact with said liquid surface at its lower peripheral edge, whereupon the weight gain m [g] is measured over time. The absorption capacity is determined as the weight gain, due to liquid absorption, at t = 1 min. The temperature is 20°C.

**[0083]** An increase of the absorption capacity is determined as the percent increase of the absorption capacity of a treated sample over a non-treated (but otherwise identical) second sample.

#### Claims

- Method for increasing the hydrophilicity of a fibrous or porous polymeric material in a sample comprising said polymeric material, said method comprising contacting said sample with an oxidizing gas comprising an oxidizing component.
- Method of claim 1, wherein said oxidizing component is atomic oxygen, ozone, or electronically excited oxygen molecule.
- Method of any one of the preceding claims, wherein said polymeric material is selected from the group

5 consisting of biopolymers, synthetic polymers, cellulose, starch, protein, polyethylene, polypropylene, polyurethane, polyterpene, inorganic polymers, phenolic resins, polyanhydrides, polyester, polyolefins, and polyalkenes, polyamide, polyacetal, polyethylene terephthalate, polycarbonate, and cellulose acetate.

- Method of claim 3, wherein said polymeric material is cellulose.
- Method of any one of the preceding claims, wherein said contacting step comprises perfusing said sample with said oxidizing gas.
- Method of any one of claim 5, wherein said perfusion is effected by a pressure difference between two opposing sides of said sample.
- Method of any one of the preceding claims, wherein said porous or fibrous polymeric material is a woven material, a non-woven material, a knitted material, a crocheted material, a spun-bonded material, melt-blown material, a foamed material, or a sintered material.
- Method of any one of the preceding claims, wherein the flux of the oxidizing component into the sample, is between 10<sup>20</sup> atoms/m<sup>2</sup>/s and 10<sup>23</sup> atoms/m<sup>2</sup>/s.
- Method of any one of the preceding claims, wherein the ratio between the flux of the oxidizing component out of the sample [atoms/m<sup>2</sup>/s] and the flux of the oxidizing component into the sample [atoms/m<sup>2</sup>/s] is between 0.1 and 0.9.
- Method of any one of the preceding claims, wherein said contacting is at a maximum temperature of between 20°C and 300°C.
- Method of any one of the above claims, wherein said contacting is in a dry state.
- A polymeric material modified by a method of any one of claims 1 to 11.
- A product comprising a polymeric material of claim 12.
- Product of claim 13, wherein said product is selected from the group consisting of diapers, incontinence products, wound dressings, medical patches, hygienic pads, sanitary towels, garment products, footwear products, sintered products, membranes, filters, implantable medical products.

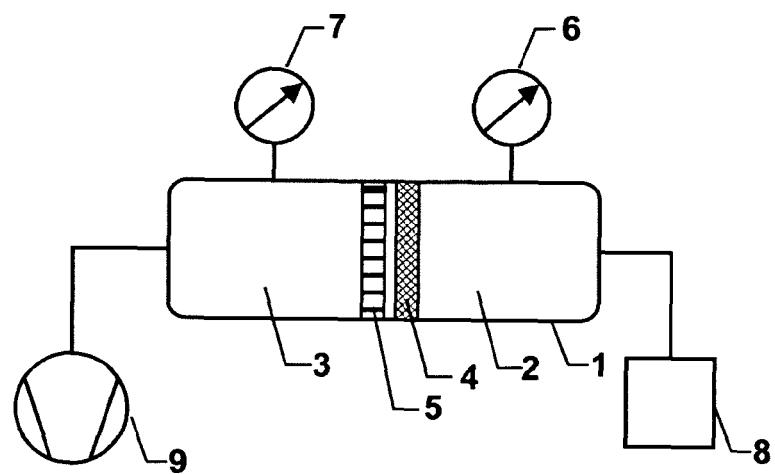


Figure 1

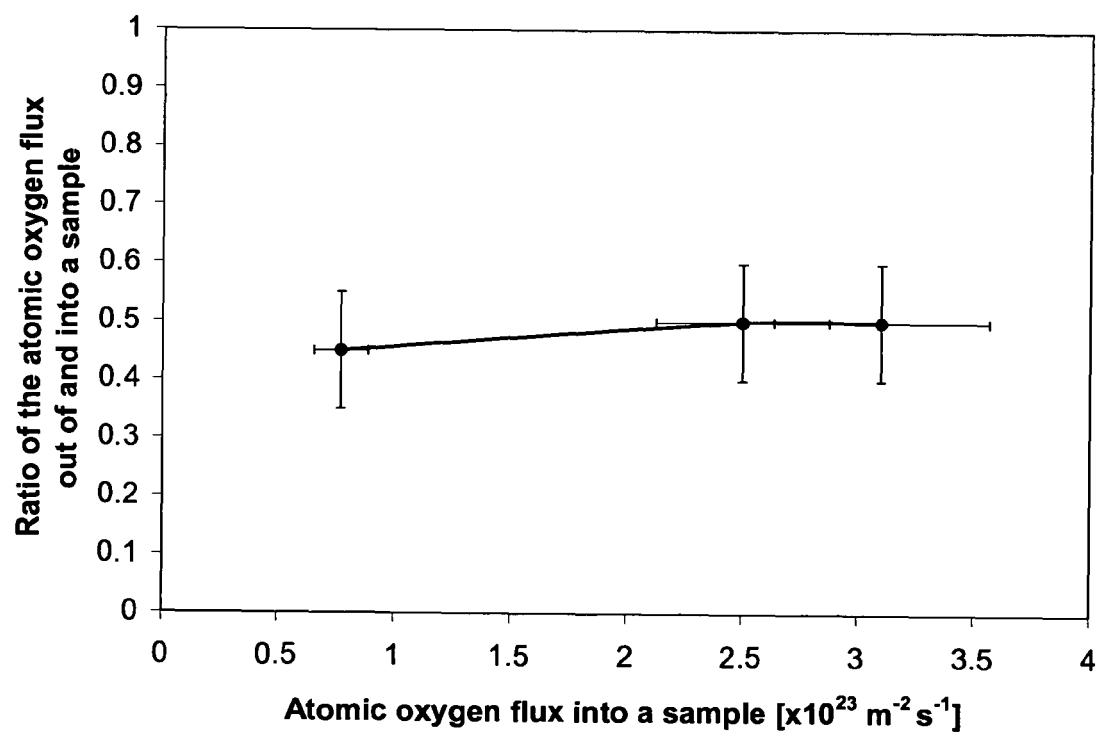


Figure 2

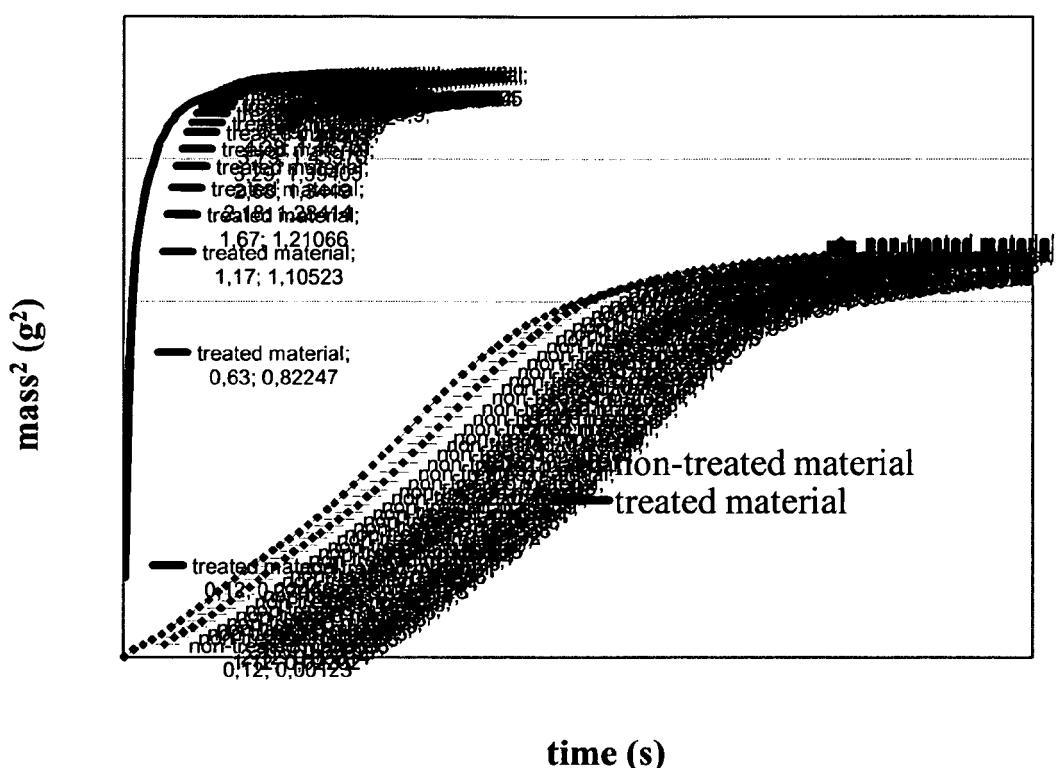


Figure 3



## EUROPEAN SEARCH REPORT

Application Number  
EP 11 00 6735

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (IPC)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	US 2011/083282 A1 (MYUNG JASON [US] ET AL) 14 April 2011 (2011-04-14) * claims * -----	1-12	INV. D06M11/32 D06M11/34 D06L3/02 D06L3/04
X	US 5 484 651 A (SASAKI KOSHI [JP] ET AL) 16 January 1996 (1996-01-16) * column 2, line 20 - column 2, line 42 * * column 3, line 64 - column 4, line 29 * * column 5, line 52 - column 6, line 20; claims * -----	1-3,5-7, 10-14	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
1	Place of search Munich	Date of completion of the search 19 January 2012	Examiner Koegler-Hoffmann, S
EPO FORM 1503 03.82 (P04C01) CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 11 00 6735

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-01-2012

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011083282	A1 14-04-2011	NONE	
US 5484651	A 16-01-1996	NONE	

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