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(54) Title: SUPERABSORBENT POLYMER COMPOSITE PARTICLE COMPRISING ACIDIC SUPERABSORBENT POLYMER AND NANOPARTICULATE CLAY MATERIAL

(57) Abstract: The present invention relates to a superabsorbent polymer composite particle comprising (A) an acidic superabsorbent polymer having free carboxylic acid groups of formula -COOH, wherein the degree of neutralization is 50% or less, preferably 40 % or less, and (B) a nanoparticulate clay material, wherein the content of the nanoparticulate clay material is greater than 0 % by weight, but less than 5 % by weight. The superabsorbent polymer composite particle shows good properties, such as permeability, capacity, gel strength and conductivity without requiring surface-crosslinking. The invention also relates to a method for preparing such a superabsorbent polymer composite particle, as well as uses thereof and disposable hygiene articles comprising it,



WO 2014/094892 A1

SUPERABSORBENT POLYMER COMPOSITE PARTICLE COMPRISING
ACIDIC SUPERABSORBENT POLYMER AND NANOPARTICULATE CLAY
MATERIAL

Introduction

The present invention is generally in the field of superabsorbent polymers (SAP), as they are generally used in many technical fields, for instance in hygiene products, such as sanitary napkins, disposable diapers, etc. Superabsorbent polymers have been increasingly used in such hygiene products due to their capability of absorbing large volumes of liquids, their easiness of manufacture, and their availability from commonly used and commercially available monomers as starting material.

Superabsorbent polymers generally have a polymer backbone and pendent hydrophilic groups that are capable of interacting with water in the liquid to be absorbed. Upon contact with water, such superabsorbent polymers take up the water and swell, thereby absorbing and retaining the liquid. A typical hydrophilic group is a carboxylic acid group, which can be present in either free form (-COOH) or in neutralized form ($\text{-COO}^-\text{M}^+$, wherein M is a cation), also known as carboxylate. A superabsorbent polymer having such carboxylic acid or carboxylate groups, such as a polyacrylate, is denoted as "acidic" superabsorbent polymer if the degree of neutralization $[\text{COO}^-\text{M}^+ / (\text{COO}^-\text{M}^+ + \text{COOH})]$ is less than 50 %.

Superabsorbent polymers have to fulfil certain requirements in order to be applicable in hygiene products, such as diapers and sanitary napkins. For instance, the superabsorbent polymer must have a high absorption capacity (absorbency) and must retain the absorbed water even under stress, as it generally occurs when the hygiene product is worn due to the movements of the wearer. These properties are reflected by the so-called "Centrifuge Retention Capacity" (CRC) and "Absorbency Under Load" (AUL). Moreover, the superabsorbent polymer must have a high porosity in order to allow the liquid to enter the superabsorbent polymer quickly. In addition, superabsorbent polymers should have a high strength (modulus), so that particles of the superabsorbent polymer do not crush and convert into a fine powder when processed and/or worn and/or stored.

In particular, leakage prevention and odour control are important aspects for absorbent articles of today. Especially for absorbent articles worn by active men and women, for example users of "Tena Lady" and "Tena for men". Active users of absorbent articles are of course extra sensitive for smell or leakages.

Nowadays, acidic SAPs are used for in such absorbent articles, since they provide better odour control than non-acidic SAPs. However, the downside with acidic SAP is that the capacity is lower for acidic SAP than for a regular SAP.

Generally, important properties for SAP-particles in an absorbent core of an absorbent article thus include:

- Capacity, as represented by CRC;
- Gelstrength, as represented by AUL; and
- Permeability, as represented by the Saline Flow Conductivity (SFC)

In view of all these requirements, the development of new and improved superabsorbent materials has been a field of active research. For instance, in order to ensure a high capacity and a high strength (modulus), superabsorbent polymers are nowadays generally surface-crosslinked in a separate production step following the synthesis of the superabsorbent polymer order to form a relatively hard shell around the superabsorbent polymer particle. Also, the use of composite material constituted by a superabsorbent polymer and other materials has been investigated in order to obtain a good balance of properties, as required for the application in hygiene products.

Yet, it is a problem today to achieve a SAP having all these above properties. A further problem is to maintain the permeability created by surface crosslinking the SAP particles. Surface crosslinking is a fairly expensive process that is done in a separate production step. When processing the SAP particles in the production machines for the absorbent article (such as a diaper), the surface of the SAP particles will be damaged when passing blowers and nozzles, and the benefit of the surface crosslinking

will be strongly reduced. Another problem is to obtain a high permeability and to prevent gel blocking, while simultaneously obtaining a high capacity and a high absorbency under load. The capacity and the absorbency under load will namely be reduced linearly with the use of bulk crosslinkers. This is an even greater issue when using an acidic SAP, due to an already low capacity combined with a higher price than for regular SAP.

Furthermore it is known to use clay particles in superabsorbent particles, and that the use of clay particles will increase the AUL of the SAP. For instance, WO 2009/041903 A1 describes a claylinked polymer gel wherein a clay mineral is incorporated into e.g. a polyacrylate polymer. The polyacrylate polymer is prepared by polymerization of acrylamide monomers, leading to polyacrylamide, which is then converted to the respective acrylate by hydrolysis under alkaline conditions using e.g. aqueous sodium acetate, leading to a polyacrylate polymer wherein the vast majority of carboxylic acid groups $-COOH$ is neutralized to carboxylate groups $-COO^- Na^+$. The composite materials described in this document contain relatively high amounts of clay material, e.g. up to 50%. Similar materials are also described in WO 2009/041870.

EP 1 829 896 A1 describes a production process of an organic/inorganic composite hydrogel composed of a polymer of a water-soluble organic monomer and a water-soluble clay mineral. The water-soluble acrylic monomer may include acrylamide derivatives.

Clay particles may crosslink the superabsorbent just as well as the bulk crosslinker. However, what is stated above for regular bulk crosslinker is valid also for the clay particles. So, high amounts of clay particles will lower the CRC and the AUL.

In the studies described in the above documents, the clay content is relatively high, oftentimes greater than 10% by weight. In addition, the superabsorbent polymers used in this study either make use of polyacrylamide as such, or acrylate polymers prepared by hydrolysis under alkaline conditions, leading to the respective acrylate polymers having pendant ionic groups of formula $-\text{COO}^-\text{M}^+$ (wherein M is generally a metal that stems from the alkaline reagent in the hydrolysis, such as sodium in case that e.g. aqueous sodium acetate is used for the hydrolysis).

Yet, there remains a need for superabsorbent composite materials that simultaneously fulfil the requirements for superabsorbent polymers, such as high strength (modulus), high permeability, good AUL and CRC values, and which are also easy to manufacture in few process steps.

Summary of the invention

The present invention has been made in view of the prior art and aims at solving the drawbacks of the prior art products. Specifically, the present invention aims at providing an SAP particle that shows good CRC, SFC and AUL, and simultaneously allows odor control.

The present invention is based on the surprising finding that the use of a low amount of clay particles as bulk crosslinker in acidic SAP will strongly affect the permeability of the SAP and give a high permeability to the SAP particles, so that a surface crosslinking is not necessary. This finding has several positive effects. The first positive effect is that - since the clay is not added to the surface, but to the bulk of the superabsorbent particle - the processing in the processing machines for the production of the absorbent article will not destroy the permeability of the SAP. The second positive effect is that since so low amount of the clay particles are needed, the AUL - and the CRC - may be kept high. Hence, both odour control and high absorption may be achieved with the present invention.

The present invention provides:

1. A superabsorbent polymer composite particle, comprising

(A) an acidic superabsorbent polymer having free carboxylic acid groups of formula $-\text{COOH}$, wherein the degree of neutralization, as expressed by the formula

$$\text{Degree of Neutralization} = \frac{[\text{amount of } -\text{COO}^-\text{M}^+ \text{ groups}]}{[\text{total amount of } -\text{COOH} \text{ groups and } -\text{COO}^-\text{M}^+ \text{ groups}]} * 100 \%$$

(wherein M is a monovalent metal cation or an ammonium cation NH_4^+), is 50% or less, preferably 40 % or less, and

(B) a nanoparticulate clay material,

wherein the content of the nanoparticulate clay material is greater than 0 % by weight, but less than 5 % by weight of the total superabsorbent polymer composite particle.

2. The superabsorbent polymer composite particle according to item 1, wherein the superabsorbent polymer does not contain any one of carboxylic acid amide groups and carboxylic acid ester groups.

3. The superabsorbent polymer composite particle according to any of items 1 and 2, wherein the content of the nanoparticulate clay material (ii) is equal to or less than 2.5 % by weight, preferably equal to or less than 1.25 % by weight, but equal to or more than 0.075 % by weight, preferably equal to or more than 0.15 % by weight of the total superabsorbent polymer composite particle.

4. The superabsorbent polymer composite particle according to any of items 1, 2, and 3, wherein the superabsorbent polymer particle is not surface-crosslinked.

5. The superabsorbent polymer composite particle according to any of items 1, 2, 3, and 4, wherein the superabsorbent particle comprises 95 % by weight or more of superabsorbent polymer.

6. The superabsorbent polymer composite particle according to any of items 1, 2, 3, 4, and 5, wherein the average particle size of the nanoparticulate clay material (B) is less than 1 μm , preferably 5 - 500 nm, more preferably 10 - 50 nm.

7. The superabsorbent polymer composite particle according to item 1, 2, 3, 4, 5, and 6, wherein the nanoparticulate clay material is selected from the group consisting of 1,1 phyllosilicates, 1,2 phyllosilicates and synthetic clays.

8. The superabsorbent polymer composite particle according to item 7, wherein the 1,1 phyllosilicates are selected from the group consisting of kaolinite, dictate and and similar compounds, wherein the 1,2 phyllosilicates are selected from the group consisting of smectites, preferably montmorillonite or saponite, micas, preferably illite, and similar compounds, and wherein the synthetic clay is selected from laponite and similar compounds .

9. The superabsorbent polymer composite particle according to item 7, wherein the nanoparticulate clay material is a synthetic clay material, preferably laponite.

10. The superabsorbent polymer composite particle according to any of items 1, 2, 3, 4, 5, 6, 7, 8, and 9 which is obtainable by polymerizing a monomer comprising a carboxylic acid moiety in a suspension of the nanoparticulate clay material in the optional presence of a crosslinking agent and an initiator.

11. The superabsorbent polymer composite particle according to item 10, wherein the monomer comprising a carboxylic acid moiety is selected from acrylic acid and methacrylic acid.

12. Use of the superabsorbent polymer composite particle according to any one of items 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11 in a disposable hygiene product.

13. Use according to item 12, wherein the disposable hygiene article is selected from a sanitary napkin, a diaper, and an incontinence guard.

14. A disposable hygiene article, preferably selected from a sanitary napkin, a diaper, and an incontinence guard, comprising a superabsorbent polymer composite particle according to any one of items 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11.

Detailed description of the invention

(A) Superabsorbent polymer

The superabsorbent polymer used in the superabsorbent polymer composite particles (in the following also referred to as "SAP composite particles") is a superabsorbent polymer having carboxylic acid groups of formula -COOH (also referred to as "free" carboxylic acid groups) and carboxylate groups of formula $\text{-COO}^-\text{M}^+$ (wherein M^+ is a monovalent cation, typically a monovalent metal cation, such as Li^+ , Na^+ , K^+ , or NH_4^+ , also referred to as

neutralized carboxylic acid groups in the present invention).

In the present invention, an acidic superabsorbent polymer is used, which denotes that 50 % or more of the total of carboxylic acid groups and carboxylate groups are free carboxylic acid groups (-COOH), i.e. that the content of carboxylate groups $\text{-COO}^-\text{M}^+$ (wherein M^+ is a monovalent cation, typically a monovalent metal cation, such as Li^+ , Na^+ , K^+ , or NH_4^+), also referred to as neutralized carboxylic acid groups in the present invention, is equal to or less than 50%, as expressed by the following formula:

$$\text{P}_{\text{COOH}} = [\text{amount of } \text{-COOH groups}] /$$
$$[\text{total amount of } \text{-COOH groups and } \text{-COO}^-\text{M}^+\text{groups}] * 100 \% \geq$$
$$50 \%$$

P_{COOH} (denoting the relative amount of free carboxylic acid groups) and the degree of neutralization (denoting the relative amount of neutralized carboxylic acid groups) thus fulfil the relation $\text{P}_{\text{COOH}} + \text{degree of neutralization} = 100\%$.

Notably, other groups not fulfilling the definition above, such as groups wherein M is not a monovalent cation or groups wherein the carboxylic acid group is modified by a group that is bound to the COO moiety by a covalent bond (such as in a carboxylic acid ester or amide) are

disregarded for the calculation of P_{COOH} and the degree of neutralization.

Thus, contrary to common superabsorbent polymers used in the art, at the most half (and typically less than half) of the carboxylic acid groups are neutralized and converted into carboxylate groups of formula $-COO^{-}M^{+}$. In other words, the degree of neutralization, as expressed by the following formula:

$$\frac{[\text{amount of } -COO^{-}M^{+} \text{ groups}]}{[\text{total amount of } -COOH \text{ groups and } -COO^{-}M^{+} \text{ groups}]} * 100 \%$$

i.e. the ratio of neutralized acid groups $-COO^{-}M^{+}$ to the total of free acid groups $-COOH$ and neutralized acid groups (carboxylate groups) of formula $-COO^{-}M^{+}$, is equal to or less than 50%, preferably 40% or less, more preferably 35% or less. Put differently, P_{COOH} is equal to or greater than 50, and preferably equal to or greater than 55, and more preferably equal to or greater than 60, such as up to 65.

While it is generally possible that all of the carboxylic acid groups are in free form and are not neutralized, i.e. that the degree of neutralization is 0% and P_{COOH} is 100, it may be difficult to achieve such a low degree of neutralization from a technical point of view, e.g. due to impurities in the starting material. Further, while a high proportion of free carboxylic acid groups is generally beneficial to achieve an odour inhibiting effect, a too

high proportion of free carboxylic acid groups (i.e. a too high value of P_{COOH}) also has an adverse effect on certain properties of the SAP particles, such as the Centrifuge Retention Capacity (CRC). It is therefore generally necessary to adjust the proportion of free carboxylic acid groups (i.e. P_{COOH}) such that a good balance of properties is obtained. Accordingly, P_{COOH} is preferably 75 or less, more preferably 70 or less, and even more preferably 65 or less, and the degree of neutralization is preferably 25 or more, more preferably 30 or more, and even more preferably 35 or more.

In view of the above, it is therefore evident that P_{COOH} is preferably adjusted within the preferred maximum and minimum values described above, such as for example in the range of e.g. 55 - 70.

The degree of neutralization and the relative amount of free carboxylic acid groups, as described above, can be determined by titration. For instance, if one wants to determine the degree of neutralization, first a sample (e.g. 1 g) of the superabsorbent polymer or the SAP composite particle is ground with a pestle and mortar to obtain a powder, and then this sample is placed in a beaker together with 100 ml of distilled water. Then, the amount of free carboxylic acid groups per gram of SAP or SAP composite particle is determined by titration with a strong base from a burette, e.g. 0.01 N aqueous sodium hydroxide, under stirring with a conventional PTFE coated magnetic stirring bar at 300 rpm. The pH is measured using a conventional pH meter, so that the neutralization

point can be determined, as is usually done for weak carboxylic acids. This procedure gives the amount of free carboxylic acid groups per gram of SAP.

In order to determine the total amount of -COOH and $\text{-COO}^-\text{M}^+$ groups, first a sample of 1 g SAP or SAP composite particle is ground with mortar and pestle and is then treated with 100 ml aqueous 0.1 N hydrochloric acid for 30 minutes at room temperature and under stirring at 300 rpm in order to convert all $\text{-COO}^-\text{M}^+$ groups into -COOH groups. Then, the material is filtered off and washed with distilled water until neutral. After drying the material at 80 °C for 10 hours in an oven, the material is weighed and transferred into a 100 ml beaker, and the amount of free carboxylic acid groups -COOH is determined as described above. This amount is the sum of the original amount of -COOH groups and those -COOH groups that were converted from carboxylate groups during the acid treatment.

Hence, from the two tests above, the number of originally present free carboxylic acid groups -COOH and the total of free carboxylic acid groups and carboxylate groups are obtained. Hence, it is possible to determine the relative amount of -COOH groups to the total of both, which in turn allows to determine the degree of neutralization.

The method above is applicable to SAP particles that contain only free carboxylic acid groups of formula -COOH and neutralized carboxylic acid groups of formula $\text{-COO}^-\text{M}^+$, as defined above. However, the method may be complicated

if additionally groups are present in the SAP particle that hydrolyze under the acidic conditions employed for converting the neutralized $\text{-COO}^-\text{M}^+$ into -COOH groups and which then, upon hydrolysis, also form -COOH groups. These groups are specifically carboxylic acid ester groups and carboxylic acid amide groups.

Accordingly, in order to avoid such a complication, the SAP particles preferably do not contain such hydrolysable groups, and in particular the SAP particles preferably do not contain carboxylic acid ester groups and carboxylic acid amide groups. However, if such groups are present, their content and their contribution to the apparent number of -COOH groups in the above method must be considered. This can for instance be achieved by determining the amount of hydrolysis products other than a -COOH group (e.g. a primary or secondary amine or ammonia in case of an acid amide, and/or a primary or secondary alcohol in the case of an ester) in the acidic solution used for converting the COO^-M^+ into -COOH groups by a conventional method. This can then be used for calculating the contribution of such other groups to the total amount of COOH groups determined by the method above, and this contribution can then be subtracted in order to calculate P_{COOH} and the degree of neutralization for only free carboxylic acid groups / groups of formula COO^-M^+ .

The superabsorbent polymer of the present invention is not particularly limited, as long as it has COOH groups and is an acidic SAP, as mentioned above. However, preferably the polymer is an acrylic polymer prepared directly from

acrylic acid or methacrylic acid, i.e. is prepared directly from a monomer composition comprising only acrylic acid and/or methacrylic acid and/or salts thereof, but no acrylamide or acrylic acid ester. In consequence, the superabsorbent polymer preferably does not contain any or no substantial amount of amide groups. In the same manner, the superabsorbent polymer preferably does not contain any or no substantial amount of ester groups.

Besides the free and neutralized carboxylic acid groups, the superabsorbent polymer may also comprise further functional groups, as long as these do not interfere with the purposes of the present invention. For instance, the superabsorbent polymer may comprise sulfonate groups, carboxylic acid ester groups and carboxylic acid amide groups. However, preferably the superabsorbent polymer is such that more than 75%, preferably 80% or more, more preferably 90% or more, and even more preferably 95 % or more of the repeating units of the superabsorbent polymer are derived from monomers that have carboxylic acid groups as the sole functional group, such as acrylic acid and methacrylic acid. Most preferably, the SAP polymer is prepared from only acrylic acid, methacrylic acid and their corresponding neutralized species also containing a monovalent cation (e.g. sodium acrylate and/or sodium methacrylate).

(B) Nanoparticulate clay material

The nanoparticulate clay material (also referred to as clay nanoparticles in the present invention) is preferably a nanoparticulate clay material selected from the group consisting of 1,1 phyllosilicates, 1,2 phyllosilicates and synthetic clays.

Examples of 1,1, phyllosilicates include kaolinite, dictate and similar compounds. Examples of 1,2 phyllosilicates include for instance the groups of smectites, micas and similar compounds. Examples of smectites include montmorillonite, saponites and similar compounds. Examples of micas are illite and similar compounds. Examples of synthetic clays include Laponite and similar compounds.

Specific further clays that may be used in the present invention include those selected from the group consisting of attapulgite, kaolinite, vermiculite, nontronite, beidellite, iron-saponite, hectorite, fluorohectorite, sauconite, stevensite, magadite, kaolin minerals (including kaolinite, dickite and nacrite), serpentine minerals, sepiolite, palygorskite, bauxite, phyllosilicate, montronite, hallosite, smectite, montmorillonite, illite, bentonite, sercite, hectorite, chlorite and combinations thereof.

Preferably, the nanoparticulate clay mineral is a synthetic mineral, more preferably Laponite, which is manufactured by Laporte industries, Charlotte, NC,. Other preferred clay minerals include the examples of 1,1, and 1,2 phyllosilicates mentioned above.

The nanoparticulate clay material generally has an average particle diameter of 1 μm or less. Preferably, the average particle diameter is 5-500 nm, more preferably 5-200 nm, even more preferably 10-50 nm. The particle diameter can be measured via a light scattering method, for example following the instructions given in O.Okay and W.Opperman, *Macromolecules* 2007, 40, 3378-3387. Preferably at least one particle dimension, such as width, length or thickness, should be in the single nanometer size range, i.e. is less than 10 nm.

The content of the nanoparticulate clay material in the SAP composite particle of the present invention is greater than 0% by weight, but less than 5% by weight of the total weight of the SAP composite particle. The content of the nanoparticulate clay material in the SAP composite particle of the present invention is thus below the contents generally used in the prior art.

As demonstrated by the Examples that will be described later, including such a low amount of a nanoparticulate clay material in the acidic SAP composite particle allows obtaining a higher strength (modulus), even without the necessity of surface-crosslinking the SAP composite particles. Moreover, within the specified content range, simultaneously good Absorbency Under Load (AUL) and Centrifuge Retention Capacity (CRC) can be obtained. Accordingly, by adjusting the content of the nanoparticulate clay material within the range of the present application, a high strength, high permeability, good AUL and good CRC can be obtained, while the SAP

composite particle is also easy to manufacture, because a separate cross-linking, as generally necessary for prior art SAP composite particles employing non-acidic SAPs, is not necessary. Put differently, by including the nanoparticulate clay material it becomes possible to omit the separate crosslinking step of the SAP, as otherwise necessary for conventional acidic SAPs.

When the nanoparticulate clay material is added in an amount of 0.10% or greater by weight with respect to the total weight of the SAP composite particle, the permeability is similar to commercial SAP, and consequently the lower limit of the content of the nanoparticulate clay material is preferably 0.10 weight% or greater, more preferably 0.15 weight% or greater.

Conversely, if the amount of nanoparticulate clay material is too high, the Absorbency Under Load and the Centrifuge Retention Capacity decrease. Accordingly, the upper limit of the content of the clay material is less than 5.0% by weight, preferably 3.0% by weight or less, further preferred 2.0% by weight or less, further preferred 1.25% by weight or less

It goes without saying that the upper and lower limits given above can be freely combined. For example, the content of the nanoparticulate clay material can be in the range of 0.15-1.25% by weight, 0.30 - 2.0 % by weight, or 0.30 - 1.25 % by weight. With regard to AUL and CRC, preferred ranges of the amount of particulate clay material include 0.10 - 1.25 % by weight, 0.15 - 2.0 % by

weight, and 0.10-2.0 % by weight. Further preferred is an amount of particulate clay material in the range of 0.15 - 0.60 % by weight, and most preferred 0.15-0.30 % by weight.

The SAP composite particle of the present invention preferably has an Absorbency under Load (AUL) of 18 g/g or greater at 0.3 psi, more preferably 21 g/g or greater at 0.3 psi, further preferably 23 g/g or greater at 0.3 psi, as determined by the method given in the Examples section.

The SAP composite particle of the present invention preferably has a CRC of 17 g/g or greater, more preferably 21 g/g or greater, and most preferably 23 g/g or greater, as determined by the method given in the Examples section.

The SAP composite particle of the present invention preferably has a permeability of 20 cm³s/g or higher, more preferably 25 cm³s/g or higher, as determined by the method given in the Examples section.

Process for producing the SAP composite particle

The SAP composite particle of the present invention is preferably produced by a so-called "direct method", wherein the composite material is prepared by adding the monomers forming the superabsorbent polymer having carboxylic acid groups, preferably acrylic acid or methacrylic acid and/or the corresponding salts thereof with monovalent cations, and optional further components are added to a suspension of the nanoparticulate clay

material. The reaction mixture may optionally also contain a cross-linking component, such as for instance N,N-methylenebisacrylamide (MBA) and an initiator. Other crosslinking agents that may be used include pentaerythritol triallyl ether, pentaerythritol triacrylate, ethylene glycol dimethacrylate, and trimethylolpropane triacrylate. Preferred initiators are redox initiators, such as such as sodium persulfate, potassium persulfate, ammonium persulfate and sodium hydrogen sulphite, and initiators capable of initiating polymerization upon heating, such as azoinitiators like azobisisobutyronitril (AIBN) or similar compounds, or irradiation.

The degree of neutralization of the carboxylic acid groups is preferably adjusted already during the preparation of the SAP composite particle. For instance, if a degree of neutralization of e.g. 30% is desired, also a respective amount of a strong base can be added already during the synthesis, allowing for neutralizing 30% of the acid groups of the employed monomer, such as acrylic acid and/or methacrylic acid. Hence, the reaction mixture may comprise, in addition to the optional cross-linker and the optional initiator, a base in a desired amount, such as e.g. 30 mole% percent of e.g. sodium hydroxide relative to the number of moles of carboxylic acid groups in the monomer composition. Of course, it is also possible to use a monomer composition wherein the carboxylic acid moiety of the monomer, such as the carboxylic acid moiety of acrylic acid and/or methacrylic acid, is already

neutralized to the desired degree before the composition is used in the synthesis of the SAP.

Alternatively, the degree of neutralization may also be adjusted after the synthesis of the SAP composite particle by conventional acid/base chemistry. For instance, it is possible to use a higher or fully neutralized carboxylic acid monomer in the above syntheses, so that initially a SAP composite particle having a higher degree of neutralization is formed. Such a SAP composite particle may then be converted to the SAP composite particle of the present invention by treating it with an acid in order to reduce the degree of neutralization, e.g. by treatment with diluted hydrochloric acid.

However, in order to make the process as simple as possible, it is preferable that the process for the preparation of the SAP composite particle of the present invention does not comprise additional steps for adjusting the degree of neutralization into free carboxylic acid groups -COOH . In other words, in a preferred embodiment the process for the manufacture of the SAP composite particle of the present invention does not contain a step of converting a chemical group into a carboxylic acid group and no treatment with acid or base after the initial polymerization.

In one preferred embodiment of the present application, the SAP composite particle is not surface-crosslinked. By including a small amount of the nanoparticulate clay material within an acidic superabsorbent polymer, the

resulting SAP composite particle already has the necessary and desired strength (modulus) and permeability even without cross-linking, contrary to prior art composite particles that do require cross-linking for achieving the necessary strength (modulus) and permeability. Accordingly, in a preferred aspect, the SAP composite particle is not surface-cross-linked.

Examples

The starting monomer composition comprised 25% (w/w) acrylic acid (AA) in water. The AA was neutralized to 40 mole% using NaOH. The bulk crosslinker N,N-methylenebisacrylamide (MBA) was used in an amount of 0,75 mole% relative to the amount of acrylic acid, and the initiator potassium persulfate in an amount of 0,1 mole %.

Specifically, the appropriate amount of clay particles (Laponite XLS) was rapidly suspended in water, and the dispersion was stirred using a magnetic stirrer for at least 30 minutes. Separately, a solution of acrylic acid was neutralized to 40 % by mixing with sodium hydroxide, leaving 60% of the free (unneutralized) carboxylic acid. Then, the partially neutralized acrylic acid was added to the clay suspension in water, and subsequently the bulk crosslinking agent and the initiator were added. The mixture was thoroughly stirred for 10 min while cooling the mixture on ice/water, and then poured into test tubes which were then sealed. The test tubes were left standing to equilibrate at room temperature for 15 minutes before the polymerization was started by placing the test tubes

in an oven at 80 °C for 6 hours. This procedure was followed in all of the Examples using different amounts of clay nanoparticles.

TABLE 1

Total volume (ml)	Acrylic acid (%) w/w	MBA (mole%)	potassium persulfate (mole%)	Neutralization of acrylic acid
50	25	0,75	0,1	40 mole%

The nanoclay particles Laponite XLS were added in different amounts from 0,075% up to 10,0% (w/w) i.e. related to the added amount acrylic acid. As reference, a similar laboratory-made SAP gel without Laponite and a commercial SAP with similar neutralization degree were used.

The test tubes containing the polymerized gels were crushed, and the gels were sliced using a sharp knife. The thin gel pieces were thoroughly dried in an oven at 50 °C for 48 hours. The pieces were subsequently milled and sieved in a size between 350 - 550 µm before being characterized. The gels were characterized using a test method for saline flow conductivity (SFC) which is described in US 5,562,646 to Goldman et al. Assembly 628 in Figure 7 in the application was however substituted to a similar apparatus described in Figure 1 in Edana method WSP 242.3 The gel layer is formed from absorbent particles swollen in 0,9 % (w/w) sodium chloride solution under a confining pressure of 2,1 kPa for 1 hour. Then the apparatus is dismantled and the PMMA cylinder which

contains the pre-swollen gel layer is put as cylinder 634 Figure 7 in US 5,562,646. This test is performed according to US 5,562,646 using 0,9 % (w/w) sodium chloride solution at 23 ° C and assesses the ability of the pre-wetted gel layer to acquire and distribute liquid. Darcy's law and steady-state method are used for determining the SFC value. See "Absorbency" ed. by PK Chatterjee, Elsevier, 1985 pages 42-43 and "Chemical Engineering" Vol II Third edition, JM Coulson and JF Richardson, Pergamon Press 1978 pages 125-127

The Centrifuge Retention Capacity (CRC) was measured according to Edana method WSP 241.3 and the Absorption Under Load (AUL) was measured according to Edana method WSP 242.3 All generated data are presented in the table 2.

TABLE 2

	Laponite (% by weight)	Permeability (cm ³ s/g)	AUL 0,3 psi (g/g)	CRC (g/g)
Example 1	0,075	11 10 ⁻⁷	23	23
Example 2	0,15	24 10 ⁻⁷	23	23
Example 3	0,3	26 10 ⁻⁷	24	23
Example 4	0,6	27 10 ⁻⁷	21	21
Example 5	1,25	19 10 ⁻⁷	21	21
Example 6	2,5	47 10 ⁻⁷	19	18
Example 7	5,0	22 10 ⁻⁷	18	17
Example 8	7,5	36 10 ⁻⁷	17	17
Example 9	10,0	53 10 ⁻⁷	16	16
Reference Laboratory made	0,0	0,0	15	31
Reference Commercial M7125 (obtained from BASF)	0,0	20 10 ⁻⁷	24	24

In addition, the material of example 1 of WO 2009/041870 A1, prepared from 13.5 g Laponite and 15 g acrylamide, followed by hydrolysis of the amide groups under basic conditions (leading to a SAP composite particle having no acidic superabsorbent polymer and a too high loading of nanoparticulate material) was prepared for comparative purposes. This material had a permeability of 0, an AUL of 7 g/g, and a CRC of 24 g/g. Accordingly, the material is far inferior to the material of the present invention with respect to AUL and permeability.

As can be seen from the above, the permeability of the SAP composite particle is similar to the commercial material when the clay content is 0.15% or greater. Yet, a big difference between the different materials is that the commercial SAP is surface cross-linked, but the ones according to the invention are not, showing that this process step can be omitted if the acidic SAP is used in combination with a low amount of nanoparticulate clay material, as in the present invention. Accordingly, the SAP particle of the present invention is comparable to commercial SAPs, yet is easier to manufacture.

There is also a general trend that the permeability increases when the amount of added clay material increases. Yet, the AUL and the CRC decrease if the amount of clay material is too high, and consequently the amount of clay material is less than 5.0% by weight in the SAP composite particle of the present invention in order to obtain the desired balance of properties.

In particular at very low clay loadings, such as in the order of 0.3% or less, simultaneously good AUL, CRC, modulus and permeability can be obtained without the need for additional process steps, e.g. for surface cross-linking.

The results above demonstrate that the SAP composite particle of the present invention has a higher strength (modulus), even without cross-linking. Accordingly, the SAP composite particle of the present application can be manufactured more easily, and is thus economically favourable.

CLAIMS

1. A superabsorbent polymer composite particle, comprising

(A) an acidic superabsorbent polymer having free carboxylic acid groups of formula -COOH , wherein the degree of neutralization, as expressed by the formula

$$\text{Degree of neutralization} = \frac{[\text{amount of } \text{-COO}^-\text{M}^+ \text{ groups}]}{[\text{total amount of } \text{-COOH} \text{ groups and } \text{-COO}^-\text{M}^+ \text{ groups}]} * 100 \%$$

(wherein M is a monovalent metal cation or an ammonium cation NH_4^+), is 50% or less, preferably 40 % or less, and

(B) a nanoparticulate clay material,

wherein the content of the nanoparticulate clay material is greater than 0 % by weight, but less than 5 % by weight of the total superabsorbent polymer composite particle.

2. The superabsorbent polymer composite particle according to claim 1, wherein the superabsorbent polymer does not contain any one of carboxylic acid amide groups and carboxylic acid ester groups.

3. The superabsorbent polymer composite particle according to any of claims 1 and 2, wherein the content of the nanoparticulate clay material (ii) is equal to or less than 2.5 % by weight, preferably equal to or less than 1.25 %

by weight, but equal to or more than 0.075 % by weight, preferably equal to or more than 0.15 % by weight of the total superabsorbent polymer composite particle.

4. The superabsorbent polymer composite particle according to any of claims 1, 2, and 3, wherein the superabsorbent polymer particle is not surface-crosslinked.

5. The superabsorbent polymer composite particle according to any of claims 1, 2, 3, and 4, wherein the superabsorbent particle comprises 95 % by weight or more of superabsorbent polymer.

6. The superabsorbent polymer composite particle according to any of claims 1, 2, 3, 4, and 5, wherein the average particle size of the nanoparticulate clay material (B) is less than 1 μm , preferably 5 - 500 nm, more preferably 10 - 50 nm.

7. The superabsorbent polymer composite particle according to claim 1, 2, 3, 4, 5, and 6, wherein the nanoparticulate clay material is selected from the group consisting of 1,1 phyllosilicates, 1,2 phyllosilicates and synthetic clays.

8. The superabsorbent polymer composite particle according to claim 7, wherein the 1,1 phyllosilicates are selected from the group consisting of kaolinite, dictate and and similar compounds, wherein the 1,2 phyllosilicates are selected from the group consisting of smectites, preferably montmorillonite or saponite, micas, preferably illite, and similar compounds, and wherein the synthetic clay is selected from laponite and similar compounds .

9. The superabsorbent polymer composite particle according to claim 7, wherein the nanoparticulate clay material is a synthetic clay material, preferably laponite.

10. The superabsorbent polymer composite particle according to any of claims 1, 2, 3, 4, 5, 6, 7, 8, and 9 which is obtainable by polymerizing a monomer comprising a carboxylic acid moiety in a suspension of the nanoparticulate clay material in the optional presence of a crosslinking agent and an initiator.

11. The superabsorbent polymer composite particle according to claim 10, wherein the monomer comprising a carboxylic acid moiety is selected from acrylic acid and methacrylic acid.

12. Use of the superabsorbent polymer composite particle according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11 in a disposable hygiene product.

13. Use according to claim 12, wherein the disposable hygiene article is selected from a sanitary napkin, a diaper, and an incontinence guard.

14. A disposable hygiene article, preferably selected from a sanitary napkin, a diaper, and an incontinence guard, comprising a superabsorbent polymer composite particle according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/076752

A. CLASSIFICATION OF SUBJECT MATTER INV. C08K3/34 A61L15/00 C08F2/44 C08F220/06 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) C08K A61L C08F		
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	DATABASE WPI Week 201042 Thomson Scientific, London, GB; AN 2010-G55699 XP002708360, & CN 101 712 785 A (LIU Y) 26 May 2010 (2010-05-26) abstract	1-14
A	----- US 2010/100066 A1 (AZAD MICHAEL M [US] ET AL) 22 April 2010 (2010-04-22) page 1, paragraph 11 page 1, paragraph 14 - page 2, paragraph 18 page 4, paragraph 60-61 ----- -/-	1-13
☒ 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	
9 August 2013	22/08/2013	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Masson, Patrick	

INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2005/239942 A1 (HERFERT NORBERT [US] ET AL) 27 October 2005 (2005-10-27) page 2, paragraph 29-32 page 3, paragraphs 36,39 claims; examples -----	1-13

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Information on patent family members

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