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(54) **Titre :** NANOCOMPOSITES SUPERABSORBANTS A BASE DE POLYSACCHARIDE ET D'ARGILE
(54) **Title:** POLYSACCHARIDE-CLAY SUPERABSORBENT NANOCOMPOSITES

(57) **Abrégé/Abstract:**

The present invention relates to absorbents or superabsorbents based on polysaccharide clay nanocomposites. More particularly, it relates to a water absorbent material for absorption of salt-containing solutions as well as blood and body fluids. The absorbent nanocomposite of the present invention absorbs well under normal pressure or under load, or for retention of these fluids, or a combination of these properties. The present invention also relates to a process for making an absorbent clay polysaccharide nanocomposite.

ABSTRACT OF THE DISCLOSURE

The present invention relates to absorbents or superabsorbents based on polysaccharide clay nanocomposites. More particularly, it relates to a water absorbent material for absorption of salt-containing solutions as well as blood and body fluids. The absorbent nanocomposite of the present invention absorbs well under normal pressure or under load, or for retention of these fluids, or a combination of these properties. The present invention also relates to a process for making an absorbent clay polysaccharide nanocomposite.

TITLE OF THE INVENTION

POLYSACCHARIDE-CLAY SUPERABSORBENT NANOCOMPOSITES

FIELD OF THE INVENTION

The present invention relates to novel superabsorbent polysaccharide-clay nanocomposites, as well as to methods for producing the same.

BACKGROUND OF THE INVENTION

Water absorbent materials such as superabsorbent polymers can be employed in various applications, such as in disposable sanitary products (for example, diapers, incontinence articles, feminine hygiene products, and absorbent dressings), household articles, sealing materials, humectants in agricultural products for soil conditioning, anti-condensation coatings, water-storing materials in agriculture/horticulture, absorbent paper products, surgical absorbents, pet litter, bandages, wound dressings and as chemical absorbents. Furthermore, they can be employed in applications related to the transportation of fresh food or seafood, and in food packaging applications.

The largest use of superabsorbent materials, however, is in disposable personal hygiene products. These products include, in order of volume of superabsorbent material used, diapers, training pants, adult incontinence products and feminine hygiene products. Of these, diapers account for over 85% of the total amount of superabsorbent material sold in 2002 (Ohmura K., *Nonwovens Industry*, 2003, 34(5), p.24). As a result, the development of superabsorbent properties in general has been focused largely on optimizing absorbency of urine.

The significant differences between the numerous fluids to be absorbed by the various disposable absorbent products, poses a substantial challenge to the manufacturers of hygiene products.

With diapers, the fluid to be absorbed is typically urine, a fluid largely composed of water, salts and nitrogenous materials such as urea. With feminine hygiene products, the fluid to be absorbed is typically menses, a complex fluid including water, mucous fluids, salts, proteins, firbrinogens, blood and cell debris (Björnberg, *Nonwovens World*, 2000, 9(2), pp 54-62). In such complex fluids, the cells and clotted materials are too large to diffuse into the network structure of the superabsorbent material. Instead, they will adsorb onto the surface of the particles of superabsorbent material. The high osmotic pressure of the partially swollen superabsorbent material will then de-water the cells and clotted materials, leading to formation of a nearly impermeable layer surrounding the superabsorbent material. This layer will seriously impede the efficacy of the superabsorbent material. The nature of the superabsorbent material used for absorbing complex fluids such as menses, should therefore be different from that used for absorbing simpler fluids such as urine.

Various approaches have been disclosed regarding the development of superabsorbent materials, capable of absorbing complex fluids such as menses. However, any improvement in the ability of these specifically designed superabsorbent materials to absorb complex fluids, was oftentimes offset by a diminishment in their ability to absorb simple fluids. Moreover, these specifically designed superabsorbent materials are often more expensive in comparison to the mass-produced superabsorbent materials developed primarily for absorbing simple fluids such as urine.

The use of chemically treated superabsorbent materials having an enhanced ability to absorb complex fluids, has been described in a number of documents (Potts *et al.* US 6,350,711; Di Luccion *et al.* WO 01/91684). While considered as being somewhat effective, these materials often involve complicated manufacturing processes, which invariably increase the cost of the resulting superabsorbent materials.

From the many approaches used to design superabsorbent materials capable of absorbing complex fluids, plant-based polymers, clays or mineral compounds have been found to be particularly useful.

There is a global demand for replacing petroleum-derived raw materials with renewable plant-based materials. The use of naturally biodegradable glass-like pregelatinized starches as absorbents for liquids has been disclosed by Le Groupe Lysac (Huppé *et al.* CA 2,308,537). However, these pregelatinized starches only absorb 8 g/g, which is too low to be useful in the hygiene industry.

The absorption characteristics of these modified starches could be attributed to amylopectin; a long molecular weight polysaccharide contained in the starch composition. It was found that amylopectin, when crosslinked, provides materials having improved absorbent characteristics (Le Groupe Lysac; Bergeron *et al.* CA 2,423,712).

Modified starches can interact synergistically with mannose containing polysaccharides, ionic polysaccharides, gelling proteins or mixtures thereof (Bergeron, CA 2,426,478). These synergistic interactions have been found to be especially useful in formulating absorbent materials.

Le Groupe Lysac (Couture *et al.*, CA 2,362,006) disclosed oligomeric polyethylene glycol crosslinked polysaccharides as being particularly useful as absorbents.

The use of galactomanans, crosslinked with borate ions, as absorbent polysaccharides, has been disclosed in a number of patents (US 4,624,868 and US 4,333,461).

Cotrell *et al.* (US 5,536,825 and US 5,489,674) teach the use of solvent purified galactomanans as absorbent polysaccharides. These polysaccharides were purified with alcohols, such as methanol or isopropanol.

Even though polysaccharide based absorbent materials are known for use in personal care products, they have not gained wide usage in such products. This is due, at least in part, to their absorbent properties being generally inferior to synthetic absorbent materials such as polyacrylates. Many of the natural-based materials tend to form soft, gelatinous masses, when swollen with a liquid. When employed in absorbent products, the presence of such soft gelatinous masses tends to prevent the transport of liquid within the fibrous matrix in which the absorbent materials are incorporated. This phenomenon is known as gel blocking. Once gel blocking occurs, subsequent insults of liquid cannot be efficiently absorbed by the product, and the product tends to leak. Furthermore, many of the natural-based materials exhibit poor absorption properties, particularly when subjected to external pressures.

Clays, and other mineral compositions such as diatomaceous earth, are environmentally friendly, naturally abundant and economic. Even though many types of clay are known for their liquid absorbing properties, their use is often restricted due to their colloidal, dispersive properties in water. Numerous prior art documents teach the use of clays in combination with other ingredients such as polymers.

Burkholder *et al.* (U.S. 3,935,363) teach that clay minerals have enhanced water-absorbing properties when flocculated into granular aggregates using small amounts of an inorganic salt solution and/or a water-soluble polymeric flocculating agent such as polyacrylic acid and then dried.

A blend of a bentonite clay (>85%) and a water swellable but water insoluble organic polymeric hydrocolloid, having improved absorbency for use in cat litter applications was disclosed by Woodrum (U.S. 4,914,066).

A dry blend of kieselguhr (diatomaceous earth) and organic gel formers (CMC, starch, dextrose, gelatin, etc.), for use in absorbent pads for food packaging was disclosed by Marx (U.S. 4,615,923).

Brander (U.S. 6,376,034 and US 5,820,955) discloses a dry blend including ionic polymers such as sodium carboxymethyl cellulose, ionic crosslinkers and clays. These blends were disclosed as being particularly useful for applications in absorbent pads in food packaging.

These clay-polysaccharide blends, even though offering synergistic performances regarding their absorption properties, do not have the absorption capacities of modified polysaccharides or synthetic polymers.

Nanocomposites constitute a relatively new class of materials. Inside nanocomposites, the mixed constituents are of nanometer size. These materials often have properties that are superior to conventional microscale composites, and can be synthesized using surprisingly simple and inexpensive techniques.

Recently, nanocomposites composed of organic polymers and inorganic compounds have attracted considerable interest due to their often-unexpected hybrid properties (Okada A. *et al. Mat. Res. Soc. Proc.*, 1990, 171, 45-50). Many attempts aimed at developing high-performance clay-polymeric nanocomposite materials for various applications, have been made.

The use of organophilic clays such as activated quarternium-18 bentonite for the absorption and deactivation of fecal proteolytic enzymes, have been disclosed by Schulz (U.S. 5,869,033). These organophilic clays were used to prevent diaper rash and were not reported as absorbent materials.

Nanocomposites, prepared by the intercalation of a polymer component into the galleries of a layered inorganic and organic homostructured layered cation exchange composition, have been disclosed by Pinnavaia *et al.* (US 6,261,640). However, these compositions have not been reported as absorbent materials.

Nanocomposites for cosmetic or pharmaceutical compositions have been disclosed by Lahanas *et al.* (US 6,042,839). Again, the nanocomposites have not been reported as absorbent materials for hygiene purposes. The cosmetic product was reported as being prepared from a hydrated powder, comprising a water-soluble carboxylated gum and clay. Lahanas *et al.* also describe a method for preparing the hydrated powder.

Starches have also been used as components for nanocomposites. Hydroxyapatite reinforced starch/ethylene-vinyl alcohol copolymer composites, were reported by Reis *et al.* (J. Adv. Polym. Technol. 1997, 16, 263). Calcined kaolin/thermoplastic starch composites were disclosed by DeCarvalho *et al.* (*Carbohydr. Polym.* 2001, 45 (2), 189-194). Montmorillonite/thermoplastic starch hybrids, were described by Park *et al.* (*Macromolecular Materials and Engineering*, 2002, 287(8), pp.553-

558, J. of Mat. Sci, 2003, 38 (5), pp. 909-915).

Starch-graft-polyacrylamide constitutes one of the superabsorbents with the highest water absorbency (Riccardo P.O., *Water-Absorbent Polymers: A Patent Survey*. J. Macromol.Sci., Rev. Macromol. Chem. Phys., 1994, 607-662 (p.634) and references cited therein). However, applications of starch-graft polyacrylamide are limited due to its high production cost and lower gel strength.

The synthesis and properties of starch-graft-polyacrylamide/clay superabsorbent composites were reported by Jihuai Wu *et al.* (Macromol. Rapid Commun., 2000, 21, (15), pp 1032-1034). The composites were synthesized using an aqueous acrylamide solution, N,N'-methylenebis(acrylamide) (crosslinker), clay mineral (bentonite, kaolinite and sercite) micropowders, starch and ceric ammonium nitrate (initiator). The so-obtained starch-graft-polyacrylamide/clay superabsorbent nanocomposites were described as possessing enhanced absorbent properties, while being cost effective. Despite their high water absorption capacity, the starch-graft-polyacrylamide/clay superabsorbent composites are not biodegradable, hypoallergenic and are not derived from renewable sources.

Unfortunately, known modified polysaccharide materials do not possess absorptive properties comparable to many of the synthetic, highly absorptive materials. This has prevented widespread use of such modified polysaccharides in absorbent personal care products. Furthermore, in addition to being prepared from synthetic, non-biodegradable sources, very few nanocomposites are designed to absorb both complex and simple fluids.

There thus remains a need to develop natural-based, highly absorbent materials suitable for general use in personal care absorbent products.

The present invention seeks to meet these and other needs.

The present invention refers to a number of documents, the content of which is herein incorporated by reference in their entirety.

SUMMARY OF THE INVENTION

The present invention relates to novel superabsorbent nanocomposites, derived from polysaccharides and hydrated clays. These novel superabsorbent nanocomposites can also be crosslinked. The present invention also relates to guar based biodegradable superabsorbent nanocomposites as fluid absorbent materials.

In one embodiment, the present invention relates to environmentally friendly absorbent or superabsorbent polysaccharide-clay nanocomposites.

In a second embodiment, the present invention relates to novel, dry, solid, fluid swellable, and fluid absorbing nanocomposites, having improved absorbent properties as well as having improved gel strength, while exhibiting minimal gel-block and minimal syneresis.

In a further embodiment, the present invention relates to fluid-swellable, fluid-insoluble nanocomposites, based on modified galactomanans.

Furthermore, the present invention relates to fluid absorbing superabsorbent nanocomposites, suitable for use in disposable sanitary material products such as for example, diapers, incontinence articles, feminine hygiene products, and absorbent dressings. Further non-limiting examples of applications for the superabsorbent nanocomposites of the present invention include their use in household articles, sealing materials, humectants for agricultural products for soil conditioning, anti-condensation coatings, bandages and surgical pads, fire-fighting techniques, absorbents for chemical spills, as water-storing materials in agriculture/horticulture/forestry, as polymeric gels for cosmetics and pharmaceuticals, and in artificial snow. Additionally, the superabsorbent nanocomposites of the present invention can also be used in applications related to the transportation of fresh food or seafood. Furthermore, the polysaccharide-clay nanocomposites of the present invention can also be used in the mining and oil industry, in detergents, as well as in the food and paper industry.

In a further embodiment, the present invention relates to an absorbent member such as an airlaid or to an absorbent core comprising a polysaccharide-clay nanocomposite as described herein. Further embodiments of the present invention relate to diapers, sanitary napkins, incontinence garments, medical devices and food pads comprising a polysaccharide-clay nanocomposite as described herein.

In addition, the present invention relates to methods for preparing superabsorbent nanocomposites from biodegradable polysaccharides and clay. More specifically, the present invention relates to methods for preparing environmentally friendly superabsorbent nanocomposites from biodegradable polysaccharides and clay.

In yet a further embodiment of the present invention, a hydrated powder is prepared by blending an aqueous dispersion or solution of guar gum with clay, adding a solution of a crosslinker agent until the mixture gels, precipitating the gel, recovering the precipitate, drying the precipitate and grinding precipitate to the desired size.

Finally, the present invention relates to a purified guar gum, crosslinked in the presence of clay or mineral compounds.

Further scope and applicability will become apparent from the detailed description given hereinafter. It should be understood, however, that this detailed description, while indication preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to novel superabsorbent nanocomposites, derived from polysaccharides and hydrated clays. These novel superabsorbent nanocomposites can also be crosslinked. Additionally, the present invention relates to a purified guar gum, crosslinked in the presence of clay or mineral compounds. The purified guar gum is crosslinked using inexpensive chemical agents. The resulting nanocomposite constitutes a novel superabsorbent material.

Biodegradable polysaccharide-clay superabsorbent nanocomposites are a new class of materials. Polysaccharide-clay nanocomposite materials have been suggested as wet and dry-strength additives in pulp and paper products, in cosmetics, as well as being useful for reducing odors associated with bodily fluids.

Clay is an environmentally friendly and naturally abundant material. Aiming at combining the biodegradability and high absorbency of polysaccharides with the strength and stability of clay, polysaccharide-clay nanocomposites were prepared. These nanocomposites were prepared using solution or melt intercalation methods. Reports on the preparation of biodegradable and/or environmentally friendly superabsorbent nanocomposites or hybrids, have been scarce at best.

The present invention relates to superabsorbent polysaccharide-clay nanocomposites capable of absorbing complex fluids. Moreover, the superabsorbent polysaccharide-clay nanocomposites of the present invention are inexpensive compared to the superabsorbent materials presently available, specifically designed to absorb complex fluids. Even though demonstrating improved absorbent characteristics for complex fluids, the polysaccharide-clay nanocomposites of the present invention remain effective in their capability to absorb simple fluids.

Clays, known as being effective odor control materials, constitute a readily available and inexpensive resource. Relatively large amounts of clay can therefore be incorporated into an absorbent article, without substantially increasing the cost.

The superabsorbent polysaccharide-clay nanocomposites of the present invention may be incorporated into absorbent personal hygiene products such as, for example, baby diapers, incontinence products, sanitary napkins and the like. They may be also used in absorbent members such as absorbent cores, airlaids or foamed structures.

The superabsorbent polysaccharide-clay nanocomposites of the present invention may also be used in several other applications such as in food pads, in agricultural and forestry applications for the retention of water in the soil and for the release of water to the roots of plants and trees; in fire-fighting techniques; in bandages and surgical pads; for the cleanup of acidic or basic solution spills, including water soluble chemical spills; as polymeric gels for the controlled release of cosmetics and pharmaceuticals (also known as drug delivery systems); and in artificial snow.

The superabsorbent polysaccharide-clay nanocomposites of the present invention may be prepared following simple procedures. In one particular embodiment, an aqueous solution or suspension of a water-soluble polysaccharide is blended to homogeneity with an aqueous dispersion of clay. Examples of such polysaccharides include, but are not limited to, starches, modified starches, amylopectin, modified amylopectin, amylose, modified amylose, chitosan, chitin, guar gum, modified guar gum, locust bean gum, tara gum, konjac gum, konjac flour, fenugreek gum, mesquite gum, aloe mannans, cellulose, modified cellulose (examples include carboxyalkylated cellulose and carboxymethyl cellulose), oxidized polysaccharides, sulfated polysaccharides, cationic polysaccharides, pectin, arabic gum, karaya gum, xanthan, kappa, iota or lambda carrageenans, agar-agar and alginates.

Particularly preferred polysaccharides include galactomannan gums. Galactomannans are naturally occurring neutral polysaccharides consisting of a poly β-(1-4)-mannose backbone, to which single D-galactopyranosyl residues are attached via α-(1-6) linkages having varying degrees of substitution (DS).

Guar gum is derived from the ground endosperm of the guar plant. The guar plant is grown extensively in the semi-arid regions of Pakistan and India. As shown below in Figure 1, the structure of guar gum comprises a random galactose substitution ratio of 1.6:1. This ratio is subject to fluctuations from crop to crop or from subspecies to subspecies (Jasinski *et al.* J. of Polym. Sci., part. B, 1996, 34, pp.1477-1488).

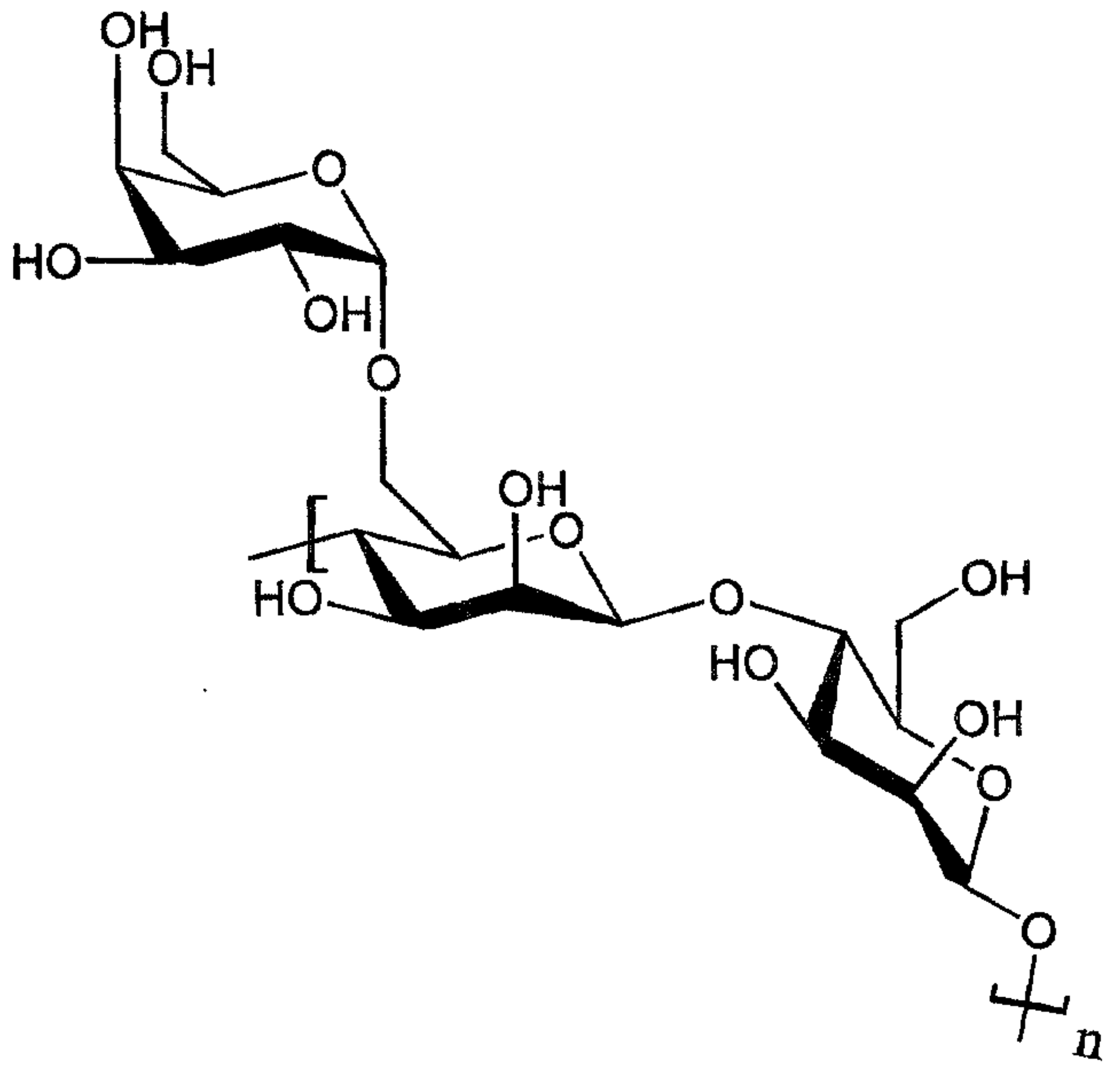


Figure 1

The clay to be used in the superabsorbent polysaccharide-clay nanocomposites of the present invention can be any clay, either natural or synthetic. Non-limiting examples of clays which can be used include, hectorites, bentonites, montmorillonites, kaolin, fullers earth, Chetos, Barasyms®, Laponites®, palygorskites, attapulgites, ripidolites, celites, smectites, vermiculites, illites, nontronites, corrensites, saponites, sepiolites, beidelites, cookeites, rectorites and diatomaceous earth.

Particularly preferred clays include bentonite. Bentonite is a montmorillonite type clay. Bentonite is principally made from colloidal hydrated aluminum silicate and contains varying quantities of iron, alkali, and alkaline earth metals. A further particularly preferred clay includes Laponite®, which is a synthetic smectic clay of the hectorite type structure (manufactured by LaPorte® industries, and distributed by RTD Chemicals).

The proportions in which the clay and polysaccharide components are to be added are not critical. However, the more effective superabsorbent polysaccharide-clay nanocomposites are obtained when the contribution of the clay component is in the range of from about 0.01:1 to about 10:1 (in dry weight) relative to the amount of polysaccharide component.

The polysaccharide component of the superabsorbent polysaccharide-clay nanocomposites of the present invention may also be crosslinked. Crosslinking will prevent the polysaccharide from completely dissolving in the suspension, by forming a polymer network. However, with too high a degree of crosslinking, any excess crosslinking agent will prevent subsequent swelling of the composite, reducing its absorbent properties.

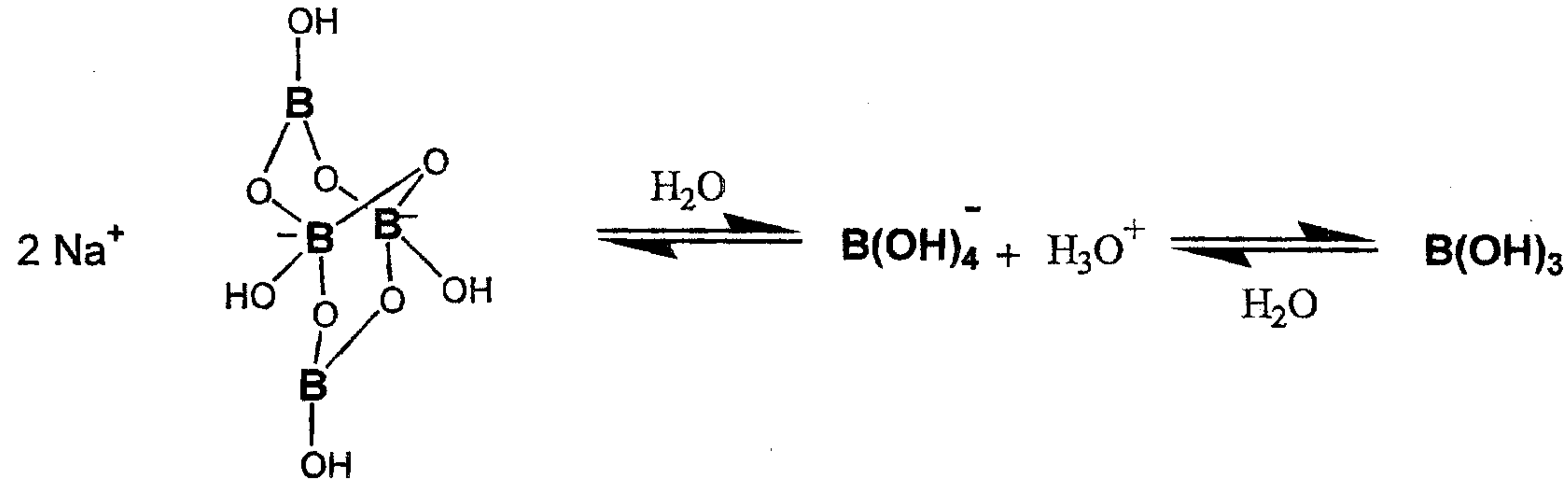
Following the mixing of the clay and polysaccharide components, a solution containing crosslinking agents is added to the mixture. Examples of crosslinking agents include, but are not limited to boric acid, borates, borax, trisodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), epichlorohydrin, succinyl dichloride, acryloyl chloride, butanedioldiglycidyl ether, ethanedioldiglycidyl ether, pyromellitic dianhydride, 1,2,3,4-butane tetracarboxylic dianhydride, and dihalogenoalkanes. Other typical covalent crosslinking agents include, but are not limited to divinylsulfones, diisocyanates, and dimethacrylates. A particularly preferred crosslinking agent is boric acid.

The crosslinked superabsorbent polysaccharide-clay nanocomposites of the present invention may also be prepared using a mixture of sodium tripolyphosphate (STPP) and sodium trimetaphosphate (STMP) as the crosslinking agent. STMP may also be used alone, as was reported for the crosslinking of amylopectin (Bergeron *et al.* CA 2,423,712).

It is to be noted that STPP can also be used alone.

Sodium tetraborate and boric acid are well-documented boron derivatives for the crosslinking of *cis*-diols, particularly for the crosslinking of guar gum (Muller US 4,624,868 and US 4,333,461). Rigidifying the macromolecular architecture of guar gum using these crosslinkers, improves its gel strength in addition to improving its absorption and retention capabilities.

Borax (sodium tetraborate) and boric acid react with guar gum via borate ions in aqueous basic solutions (Pezron E. *et al.* *Macromolecules*, 1988, 21, 1121-1125). As shown below in Scheme 1, an aqueous solution of borax consists of a system wherein borax, borate ion and boric acid are in equilibrium. ^{11}B NMR studies of a guar-borate derivative, illustrated the presence of a 2:1 complex of a five-membered mannosyl-borate ring and a six-membered galactosyl-borate ring (Jasinski R. *et al.,* J. Polym. Sc. Part B-Polym. Phys., 1996, 34, 1477-1488).



Scheme 1

After the addition of the crosslinking agent, the combined components are left for a period of time sufficient to permit gelling. Under optimal conditions of concentration, and in absence of inhibitors, typical gelling periods are not more than about 30 minutes. The mixture at this point is quite thick and requires further processing. In order to achieve the desired consistency, the gelled product is precipitated in an excess of alcohol. Other precipitation or drying techniques can also be used.

The incorporation of a precipitation step, using an alcohol such for example methanol, ethanol, or isopropanol is preferred. The alcohol precipitation step also removes impurities from the nanocomposite material. Moreover, a pH adjustment will improve the texture of the obtained superabsorbent polysaccharide-clay nanocomposite, as well as improving its aseptic properties. The product is thereafter removed by filtration, homogenized by grinding or milling to a particle size consistent with a powdery texture. The nanocomposite product can then be further processed, depending on its intended end use.

The superabsorbent polysaccharide-clay nanocomposites of the present invention are prepared via different methods, as illustrated in Examples 1 to 19. These materials are characterized by their Free Swell Capacity (FSC), their Centrifuge Retention Capacity (CRC) and their Absorption Under Load (AUL) capacity at 0.3 PSI (2,06 KPa). The FSC and CRC are standard methods in the field of superabsorbents for all applications in personal hygiene. The AUL is a standard test in the baby diaper industry.

Definitions

FSC: Free Swell Capacity, also called Absorption, refers to the amount (g) of fluid absorbed (0.9% Weight/Weight NaCl solution, thereafter called 0.9% NaCl solution or saline) per gram of the composition.

CRC: Centrifuge Retention Capacity, also called Retention, refers to the amount (g) of fluid (0.9% NaCl solution) retained by the solid under a centrifuge force, per gram of the composition.

AUL: Absorption Under Load at 0.3 PSI (2.06 KPa), also called Absorption Against Pressure, refers to the amount (g) of substance absorbed (0.9% NaCl solution) per gram of the composition, under a pressure of 0.3 PSI, using 0.9 g of absorbent in the apparatus.

Starting Materials

Split guar gums were purchased from TIC-Gum and Polypro. White bentonite 300 (supplied by Fordamin Company Ltd.), gray bentonite and Celite (supplied by Aldrich) were used. Research grade methanol, sodium hydroxide, boric acid, trisodium trimetaphosphate, sodium tripolyphosphate, hydrochloric acid, were all obtained from Sigma-Adrich Chemicals.

Test methods

AUL measurements

The Absorption Under Load (AUL) in a 0.9% NaCl solution at 0.3 psi was determined according to the recommended test method 442.2-02 from EDANA[1], using 0.9 gram of the absorbent in the apparatus.

FSC and CRC measurements (using tea bags)

Tea bags (10 X 10 cm) were made from heat sealable Ahlstrom filter paper (16.5 ±0.5) g/m^2.

FSC measurements

The Free Swell Capacity (FSC) in a 0.9% NaCl solution was determined according to the recommended test method 440.2-02 from EDANA.[2]

CRC measurements

The Centrifuge Retention Capacity (CRC) in a 0.9% NaCl solution was determined according to the recommended test method 441.2-02 from EDANA.[3]

The present invention is illustrated in further detail by the following non-limiting examples.

EXAMPLES

GENERAL PROCEDURE

Guar/clay borate superabsorbent nanocomposites were synthesized as follows:

A clay suspension was prepared by hydrating clay in distilled water at 50°C. Dried guar split was dispersed in basic aqueous solution (10% W/V NaOH), in a round-bottomed flask equipped with a mechanical stirrer. The solution was heated to 70°C under stirring, to form a guar slurry. The clay suspension was added to the guar slurry and the resulting mixture was allowed to react for one hour. A boric acid solution was then added to the mixture under stirring, resulting in the immediate formation of a hydrogel. The guar/clay composite slurry was precipitated in excess methanol. The methanol solution was neutralized (pH 7.5) with hydrochloric acid. The precipitated product was filtered and dried in an oven at about 60°C over a period of about 24 hours; until the weight of the product remained constant. The product was finally ground to provide a powdered superabsorbent nanocomposite.

EXAMPLE 1

Optimized guar-borate/Gray bentonite nanocomposite
10% bentonite

Guar split (3.00 g; 1 eq.) was suspended in deionized water (150 ml) and stirred with a magnetic stirrer. Sodium hydroxide (30% W/V; 3.0 ml; 1.22 eq.) was added and the mixture heated at 60°C for 5 hours. Meanwhile, a clay suspension (Grey Bentonite, Aldrich) was prepared by hydrating clay (0.334 g) in distilled water (10 mL) at 50°C. The clay suspension was added to the guar slurry and allowed to react for one hour. Boric acid (0.3664 g; 0.32 eq), dissolved in deionized water (20 mL), was then added with stirring. After 25 minutes of stirring without heating, the so-formed gel was blended with an excess of methanol (200 mL), triturated, and transferred into a beaker. The pH was adjusted to 7.91 under vigorous mechanical stirring using hydrochloric acid (10%). The obtained solid was filtered, washed with methanol (3 X 25 ml), dried overnight in an oven at 60°C, and ground in a coffee grinder to provide a white powder.

Performance analysis

Guar-borate/bentonite 10% bentonite	Values
CRC (g/g)	91
FSC (g/g)	115
AUL (0,3 psi 0.9g) (g/g)	11.0
pH of the gel	7.4

EXAMPLES 2-9

Guar-borate/White bentonite nanocomposites

Concentration effects of clay on performances

The guar-bentonite nanocomposites of examples 2-9 were prepared using the same method as previously described in example 1. White bentonite 300 (Fordamin Company Ltd.) was used instead of the previously used gray bentonite. Different bentonite concentrations were used as illustrated in Table 1. In example 2, no bentonite was used. All percentages illustrated in Table 1 are expressed in weight of white bentonite per weight of guar.

Table 1: Performances of guar-borate/white bentonite nanocomposites with various concentrations of bentonite

Example Number	White Bentonite Concentration (% W/W)	CRC (g/g)	FSC (g/g)	AUL (0,3 psi 0.9g) (g/g)	pH of the gel
2	0 %	93	115	10.8	7.4
3	3 %	95	113	10.1	7.4
4	5 %	90	114	11.1	7.4
5	10 %	74	101	9.8	7.4
6	15 %	73	101	9.8	7.4
7	20 %	76	107	9.7	7.4
8	30 %	60	80	8.1	7.4
9	40 %	61	65	7.8	7.4

EXAMPLE 10

Optimized guar-phosphate/Gray bentonite nanocomposite 10% bentonite

Guar split (5.0 g) was suspended in deionized water (167 mL) and stirred with a magnetic stirrer. Meanwhile, a suspension of clay (Gray Bentonite, Aldrich) was prepared by hydrating clay (0.56 g) in distilled water (10 mL) at 50°C. The clay suspension was added to the guar slurry and allowed to react for one hour. Sodium hydroxide (30%; 6.0 mL; 1.46 eq.) was added followed by sodium tripolyphosphate (STPP; 0.16 g; 0.0141 eq.) and the mixture heated at 70°C for 15 hours. After cooling to room temperature, the so-obtained gel was blended with methanol (200 ml), triturated, and the pH adjusted to 7.41 using hydrochloric acid (10%).

The obtained solid was filtered, washed with methanol (3 X 50 ml), dried overnight in an oven at 60°C, and ground in a coffee grinder to provide a white powder.

Performance analysis

Guar-phosphate/bentonite 10% bentonite	Values
CRC (g/g)	39
FSC (g/g)	48
AUL (0,3 psi 0.9g) (g/g)	9.0
pH of the gel	7.4

EXAMPLES 11-14

Guar-phosphate/Gray bentonite nanocomposites

Concentration effects of clay on performances

The guar-bentonite nanocomposites of examples 11-14 were prepared using the same method and reagents as described in example 10. Different bentonite concentrations were used as illustrated in Table 2. Example 11 was prepared without any bentonite. All percentages illustrated in Table 2 are expressed in weight of gray bentonite per weight of guar.

Table 2: **Performances of Guar-Phosphates Grey-Bentonite Nanocomposites with various concentrations of Bentonite**

Example Number	Grey Bentonite Concentration (% W/W)	CRC (g/g)	FSC (g/g)	AUL (0,3 psi 0.9g) (g/g)	pH of the gel
11	0 %	48	61	9.4	7.4
12	20 %	37	51	10.0	7.4
13	30 %	19	29	10.0	7.4
14	40 %	17	22	10.0	7.4

EXAMPLES 15-19

Optimized guar-borate/Celite nanocomposite

Guar-Celite nanocomposites were prepared using the same method as previously described in example 1. Gray bentonite was replaced by Celite (Aldrich). Different celite concentrations were used as illustrated in Table 3. Example 2 was cited as comparative example. All percentages illustrated in Table 3 are expressed in weight of celite per weight of guar.

Table 3: **Performances of guar-borate celite nanocomposites with various concentrations of celite**

Example Number	Celite Concentration (% W/W)	CRC (g/g)	FSC (g/g)	AUL (0,3 psi 0.9g) (g/g)	pH of the gel
2	0 %	93	115	10.8	7.4
15	10%	93	94	11.7	7.4
16	20 %	57	95	10.0	7.4
17	30 %	43	83	9.2	7.4
19	40 %	28	58	8.4	7.4

Although the present invention has been described hereinabove by way of preferred embodiments thereof, it can be modified without departing from the spirit and nature of the subject invention as defined in the appended claims.

REFERENCES

1. EDANA, Absorbency Against Pressure No. 442.2-02, Recommended Test Method: Superabsorbent materials-Polyacrylate superabsorbent powders-Gravimetric Determination of Absorption under Pressure, 2002.

2. EDANA, Free Swell Capacity No. 440.2-02, Recommended test Method: Superabsorbent materials-Polyacrylate superabsorbent powders-Free Swell Capacity in Saline by Gravimetric Determination, 2002.

3. EDANA, Centrifuge Retention Capacity No. 441.2-02, Recommended Test Method: Superabsorbent materials-Polyacrylate superabsorbent powders-Determination of Fluid Retention Capacity in Saline Solution After Centrifugation, 2002.

CLAIMS:

1. An absorbent material consisting of a polysaccharide clay nanocomposite material

2. An absorbent material as defined in claim 1, wherein the polysaccharide is selected from the group consisting of cellulose, modified cellulose, starch, modified starches. amylopectine, modified amylopectin, amylose, modified amylose, chitosan, chitin, guar gum, modified guar gum, locust bean gum, tara gum, konjac gum, konjac flour, fenugreek gum, mesquite gum, aloe mannans, carboxyalkylated cellulose, carboxymethyl cellulose, oxidized polysaccharides, sulfated polysaccharides, cationic polysaccharides, pectin, arabic gum, karaya gum, xanthan, kappa, iota or lambda carrageenans, agar-agar, alginates and combination thereof.

3. An absorbent material as defined in claim 2, wherein the polysaccharide is guar.

4. An absorbent material as defined in claim 1, wherein the polysaccharide clay nanocomposite is crosslinked.

5. An absorbent material as defined in claim 4, wherein the polysaccharide clay nanocomposite is crosslinked with crosslinker agents selected from the group consisting of boric acid, borates, borax, trisodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), epichlorohydrin, succinyl dichloride, acryloyl chloride, butanedioldiglycidyl ether, ethanedioldiglycidyl ether, pyromellitic dianhydride, 1,2,3,4-butane tetracarboxylic dianhydride, divinylsulfones, diisocyanates, dimethacrylates, dihalogenoalkanes and combination thereof.

6. An absorbent material as defined in claim 5, wherein the crosslinker agent is selected from the group of boric acid, borax, trisodium

trimetaphosphate, sodium tripolyphosphate and combination thereof.

7. An absorbent material as defined in claim 1, wherein the clay is selected from the group consisting of. hectorites, bentonites, montmorillonites, kaolin, Fullers earth, Chetos, Barasyms®, Laponites®, palygorskites, attapulgites, ripidolites, smectites, vermiculites, illites, nontronites, corrensites, saponites, sepiolites, celites, beidelites, cookeites, rectorites, diatomaceous earth and combination thereof.

8. A blood or menses absorbent member containing an absorbent material as described in claim 1, cellulosic fibers, synthetic fibers or a mixture thereof.

9. A sanitary napkin containing an absorbent material as described in claim 1, containing an absorbent member described in claim 8, or a combination thereof.

10. A medical device containing an absorbent material as described in claim 1, containing an absorbent member described in claim 8, or a combination thereof.

11. A urine, physiological fluid or liquid feces absorbent member containing an absorbent material as described in claim 1, cellulosic fibers, synthetic fibers or a mixture thereof.

12. A diaper containing an absorbent material as described in claim 1, containing an absorbent member described in claim 11 or a combination thereof.

13. An incontinence garment containing an absorbent material as described in claim 1, containing an absorbent member described in claim 11 or a combination thereof.

14. A food fluid absorbent member containing an absorbent material as described in claim 1, cellulosic fibers, synthetic fibers or a mixture thereof.

15. A food pad containing an absorbent material as described in claim 1, containing an absorbent member described in claim 14 or a combination thereof.

16. A composition comprising an absorbent material as defined in claim 1, wherein the composition utilisations are selected from the group consisting of artificial snow, drug delivery, cosmetic, cat litter absorbent, soil humidity retaining agent and fire retarding agent

17. A process for producing an absorbent polysaccharide-clay nanocomposite consisting of the following steps:

a) Preparing a polysaccharide solution A by dissolving the polysaccharide in a sodium hydroxide solution

b) Preparing a clay suspension B by mixing a clay in water

c) Mixing the polysaccharide solution A and the clay suspension B

d) Crosslinking the mixture A-B with a crosslinker

e) Precipitating the crosslinked mixture A-B with an organic water miscible solvent.

f) Neutralizing the crosslinked mixture A-B to a pH of 7.5

h) Recovering the precipitated crosslinked mixture A-B with a filtration process

i) Drying the crosslinked mixture A-B

j) Grinding the crosslinked mixture A-B