BIODEGRADABLE SUPERABSORBENT POLYMERS AND ABSORBENT PRODUCTS CONTAINING THEM

FIELD OF THE INVENTION

[0001] The present invention relates to biodegradable superabsorbent polymers, methods for their preparation, and their use in absorbent products such as baby diapers, adult incontinence items, feminine hygiene products, and bandages.

BACKGROUND OF THE INVENTION

[0002] Absorbent products for absorbing bodily fluids, such as baby diapers, adult incontinence items, female hygiene products, and bandages, typically comprise an absorbent core arranged between a liquid-impermeable first layer and a second layer made from a non-woven material. The absorbent core usually contains a superabsorbent polymer, either alone or mixed with fibers.

[0003] Superabsorbent polymers are polymers capable of absorbing many times their own weight in liquid. Currently, commercially available superabsorbent polymers are almost exclusively acrylic-based products, such as acrylic acid grafted onto a carrier or cross-linked polyacrylic acid. While these polyacrylic superabsorbent polymers have good absorption properties, they have the significant disadvantage of not being readily biodegradable, leading to environmental concerns.

[0004] Document D1 discloses a biodegradable superabsorbent polymer consisting of a cross-linked mixture of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) for use as a soil conditioner. The cross-linking can be performed using various cross-linking agents, including carbodiimides. However, D1 does not specifically focus on the use of carbodiimides as cross-linking agents, nor does it disclose the specific process parameters required to obtain superabsorbent polymers suitable for absorbent products designed for bodily fluids.

[0005] Document D2 discloses absorbent products comprising an absorbent core containing cellulosic fibers and polyacrylic superabsorbent polymer granules. While D2 recognizes the importance of softness in absorbent products, it relies on non-biodegradable polyacrylic superabsorbent polymers.

[0006] There remains a need for biodegradable superabsorbent polymers suitable for use in absorbent products for bodily fluids, with properties comparable to or better than traditional polyacrylic superabsorbent polymers.

SUMMARY OF THE INVENTION

[0007] The present invention addresses this need by providing biodegradable superabsorbent polymers resulting from the cross-linking of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) with a carbodiimide as cross-linking agent, methods for their preparation, and absorbent products containing these polymers.

[0008] The superabsorbent polymers of the invention provide excellent absorption capacity, water retention, and mechanical properties. Furthermore, absorbent products incorporating these polymers exhibit surprisingly improved softness compared to products using conventional polyacrylic superabsorbent polymers.

[0009] In one aspect, the invention provides a superabsorbent polymer comprising a cross-linked mixture of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC), wherein the cross-linking is achieved using a carbodiimide cross-linking agent, particularly 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC).

[0010] In another aspect, the invention provides a method for preparing a superabsorbent polymer, comprising: (i) reacting an aqueous solution of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) with a carbodiimide cross-linking agent in the presence of an acid catalyst to produce a polymer gel; (ii) washing the gel with water; and (iii) drying the gel by phase inversion.

[0011] In yet another aspect, the invention provides an absorbent product comprising a liquid-impermeable first layer, a second layer made from a non-woven material, and an absorbent core arranged between the first and second layers, wherein the absorbent core comprises a superabsorbent polymer according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The superabsorbent polymer of the invention comprises a cross-linked mixture of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC), wherein the cross-linking is achieved using a carbodiimide cross-linking agent.

[0013] Carbodiimides are unconventional cross-linking agents that induce the formation of ester bonds between CMCNa and HEC without participating in a bond themselves. During the cross-linking reaction, the carbodiimides are transformed into urea derivatives. It has been confirmed experimentally that no trace of carbodiimide remains in the final product.

[0014] A particularly preferred carbodiimide is 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC).

[0015] The weight ratio of CMCNa to HEC in the superabsorbent polymer is from 0.5 to 5.0, preferably from 0.6 to 3.2. This range of weight ratios ensures that the polymer has excellent absorption capacity, water retention, and mechanical properties.

[0016] The superabsorbent polymer preferably has a degree of cross-linking of from 2 to 10%, measured according to Italian Standard ITNA0011 published in 1990. This degree of cross-linking is essential for a useful superabsorbent polymer.

[0017] The method for preparing the superabsorbent polymer of the invention comprises the following steps: (i) reacting an aqueous solution of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) with a carbodiimide cross-linking agent in the presence of an acid catalyst to produce a polymer gel; (ii) washing the gel with water; and (iii) drying the gel by phase inversion.

[0018] In step (i), the pH is typically from 3 to 6, preferably from 3.5 to 4.5. Any acid can be used as the acid catalyst, with citric acid being typically used.

[0019] The sum of the concentrations of CMCNa and HEC in the aqueous solution is from 3 to 10 wt.%, preferably from 4 to 9 wt.%. It has been shown experimentally that concentrations below 3 wt.% or above 10 wt.% impede cross-linking.

[0020] The weight ratio of CMCNa to HEC in the aqueous solution is from 0.5 to 5.0, preferably from 0.6 to 3.2.

[0021] The concentration of carbodiimide in the solution is from 5 to 15 wt.%, preferably from 5 to 10 wt.%. It is essential that the concentration of carbodiimide falls within this range; otherwise, a gel with very poor mechanical properties is obtained.

[0022] In step (ii), the gel is preferably washed with deionized water, as this results in polymers with higher absorption capacity.

[0023] In step (iii), the phase inversion drying involves contacting the gel with a liquid that does not dissolve the polymer but will absorb water. The polymer gel is contacted with the liquid until it precipitates as white granules. The liquid used in this step is typically acetone. Drying the superabsorbent polymer by phase inversion results in a much higher absorption capacity than air drying, although air drying can also be used if necessary.

[0024] The superabsorbent polymer made by the method described above is in the form of white granules. These granules can be used to form an absorbent product by conventional methods. For example, the granules can be mixed with fibers in hot air in a rotating vacuum drum to make an absorbent core. The absorbent core can then be laminated between a liquid-impermeable first layer and a second layer made from a non-woven material as it leaves the drum to form the absorbent product.

[0025] The absorbent products of the invention comprise a liquid-impermeable first layer, a second layer made from a non-woven material, and an absorbent core arranged between the first and second layers. The absorbent core comprises the superabsorbent polymer of the invention, either alone or mixed with fibers. When fibers are present, they preferably constitute from 50 to 90 wt.% of the absorbent core, with the superabsorbent polymer constituting the remainder.

[0026] The fibers used in the absorbent core are preferably cellulosic fibers, such as cotton fibers, flax fibers, or rayon fibers. However, synthetic fibers such as polypropylene or polyamide fibers can also be used.

[0027] The absorbent products of the invention have excellent absorption capacity and water retention. Furthermore, they exhibit surprisingly improved softness compared to products using conventional polyacrylic superabsorbent polymers, particularly when cellulosic fibers are used in the absorbent core.

EXAMPLES

Example 1:

[0028] A number of superabsorbent polymers were made and compared with Superwet A1000, a commercially available polyacrylic superabsorbent polymer. The polymers were evaluated by measuring their absorption capacity, water retention, and shear modulus in accordance with the test methods published in US-A-3 000 000. The absorption capacity is a measure of the amount of liquid that can be absorbed. The water retention measures how much of the liquid is retained under moderate load. The shear modulus is an indication of how likely it is that the polymer granules will break. Acceptable products require an absorption capacity of at least 25 g H_2O per g of polymer, a water retention of at least 60%, and a shear modulus of at least 2 MPa.

[0029] The cross-linked carboxymethylcellulose/hydroxyethylcellulose superabsorbent polymers were made using the following method:

[0030] An aqueous solution containing CMCNa and HEC was prepared. The sum of the concentrations of these two components was set to be 5 wt.%. The weight ratio of CMCNa to HEC is as indicated in Table 1. The carbodiimide (EDC) cross-linking agent was added until its concentration was 7 wt.% in the aqueous solution. Citric acid was then added as a catalyst giving rise to a solution of a pH of 4.0. The gel obtained was washed with deionized water and then dried by phase inversion in acetone until it precipitated as white granules.

[0031] The properties of Superwet A1000, a commercially-available polyacrylic superabsorbent polymer, were also determined: an absorption capacity of 45 g H_2O/g polymer, a water retention of 65%, and a shear modulus of 3.0 MPa were the measurements obtained.

[0032] The CMCNa/HEC polymers of the invention all have a degree of cross-linking of 5%. The results for the CMCNa/HEC superabsorbent polymers are presented in Table 1:

Table 1:

Sample Number	CMCNa to HEC wt. Ratio	Absorption Capacity g H_2O per g polymer	Water retention %	Shear Modulus MPa
1	0.6	32	71	2.4
2	0.8	36	60	3.2
3	1.0	34	61	3.1
4	1.2	39	65	3.0
5	1.4	36	77	2.9
6	1.6	38	75	3.1
7	1.8	36	69	3.2
8	2.0	60	70	3.0
9	2.2	59	69	2.9
10	2.4	69	72	2.8
11	2.6	72	67	3.3
12	2.8	70	69	3.2
13	3.0	73	61	3.1
14	3.2	34	65	2.4

[0033] The CMCNa/HEC superabsorbent polymers all exhibit excellent properties and are all very useful. The choice of superabsorbent polymer to use will depend on the precise product being made.

Example 2:

[0034] Absorbent products were prepared using the CMCNa/HEC superabsorbent polymers of sample 4 and sample 11 from example 1, and using Superwet A1000 (a polyacrylic superabsorbent polymer).

[0035] A stream of cotton fibers in hot air was fed into a rotating vacuum drum. Superabsorbent polymer granules were fed into the stream. The absorbent core obtained is laminated between a liquid-impermeable first layer and a second layer made from a non-woven material.

[0036] The absorbent core contains 30 wt.% of superabsorbent polymer. The absorption capacity and water retention of the absorbent product were measured as described in US-A-3 000 000. The perceived softness is evaluated by a group of testers on a scale of 1 to 100. The higher the value the better and the more comfortable the absorbent product will feel to the user. The test results are presented in Table 2:

Table 2:

Superabsorbent polymer used	**CMCNa/HEC superabsorbent polymer of Sample 4**	**CMCNa/HEC superabsorbent polymer of Sample 11**	**Polyacrylic superabsorbent polymer Superwet A1000**
Absorption Capacity g H_2O per g polymer	65	95	80
Perceived Softness	80	72	31
Water retention %	65	70	72

[0037] These experiments were repeated with the sole difference that the cotton fibers were replaced by other cellulosic fibers, namely flax fibers and rayon fibers. Similar results were obtained. Although the granules of superabsorbent polymer are located within the core of the absorbent product, the nature of the polymer used appears to significantly affect the perceived softness.

[0038] In a further series of experiments, the cellulosic fibers were replaced by synthetic fibers made from polypropylene or polyamide. In this case, the perceived softness for all three superabsorbent polymers was very similar.

CLAIMS

1. A superabsorbent polymer comprising a cross-linked mixture of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC), wherein the cross-linking is achieved using a carbodiimide cross-linking agent.
2. The superabsorbent polymer according to claim 1, wherein the carbodiimide cross-linking agent is 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC).
3. The superabsorbent polymer according to claim 1 or 2, wherein the weight ratio of CMCNa to HEC is from 0.5 to 5.0.
4. The superabsorbent polymer according to claim 3, wherein the weight ratio of CMCNa to HEC is from 0.6 to 3.2.
5. The superabsorbent polymer according to any one of claims 1 to 4, wherein the degree of cross-linking is from 2 to 10%.
6. A method for preparing a superabsorbent polymer comprising: (i) reacting an aqueous solution of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) with a carbodiimide cross-linking agent in the presence of an acid catalyst to produce a polymer gel; (ii) washing the gel with water; and (iii) drying the gel by phase inversion.
7. The method according to claim 6, wherein the carbodiimide cross-linking agent is 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC).
8. The method according to claim 6 or 7, wherein the pH in step (i) is from 3 to 6.
9. The method according to claim 8, wherein the pH in step (i) is from 3.5 to 4.5.
10. The method according to any one of claims 6 to 9, wherein the acid catalyst is citric acid.

11. The method according to any one of claims 6 to 10, wherein the sum of the concentrations of CMCNa and HEC in the aqueous solution is from 3 to 10 wt.%.

12. The method according to claim 11, wherein the sum of the concentrations of CMCNa and HEC in the aqueous solution is from 4 to 9 wt.%.

13. The method according to any one of claims 6 to 12, wherein the weight ratio of CMCNa to HEC in the aqueous solution is from 0.5 to 5.0.

14. The method according to claim 13, wherein the weight ratio of CMCNa to HEC in the aqueous solution is from 0.6 to 3.2.

15. The method according to any one of claims 6 to 14, wherein the concentration of carbodiimide in the solution is from 5 to 15 wt.%.

16. The method according to claim 15, wherein the concentration of carbodiimide in the solution is from 5 to 10 wt.%.

17. The method according to any one of claims 6 to 16, wherein the gel is washed with deionized water in step (ii).

18. The method according to any one of claims 6 to 17, wherein the phase inversion in step (iii) is performed using acetone.

19. An absorbent product comprising a liquid-impermeable first layer, a second layer made from a non-woven material, and an absorbent core arranged between the first and second layers, wherein the absorbent core comprises a superabsorbent polymer according to any one of claims 1 to 5.

20. The absorbent product according to claim 19, wherein the absorbent core further comprises fibers.

21. The absorbent product according to claim 20, wherein the fibers are cellulosic fibers.

22. The absorbent product according to claim 21, wherein the cellulosic fibers are selected from cotton fibers, flax fibers, and rayon fibers.

23. The absorbent product according to any one of claims 19 to 22 in the form of a baby diaper, an adult incontinence item, a female hygiene product, or a bandage.

24. The use of a superabsorbent polymer according to any one of claims 1 to 5 in an absorbent product for absorbing bodily fluids.

25. The use of the superabsorbent polymer according to any one of claims 1 to 5 for improving the softness of an absorbent product.