Title of the Invention: Biodegradable Superabsorbent Polymers, Method for Their Preparation, and Absorbent Products Containing Them

Field of the Invention
The present invention relates to biodegradable superabsorbent polymers, a method for their preparation, and absorbent products, such as baby diapers, adult incontinence items, female hygiene products, and bandages, containing these polymers.
Background of the Invention
Superabsorbent polymers (SAPs) are materials capable of absorbing and retaining large quantities of liquid relative to their own mass. They are widely used in disposable absorbent products. Currently, the most common SAPs are polyacrylic-based products. A significant drawback of these polyacrylic SAPs is their very slow biodegradation rate, leading to environmental concerns. Many countries restrict the inclusion of non-biodegradable materials in certain compositions, such as soil improvers.
Document D1 discloses a biodegradable superabsorbent polymer for soil conditioning, which is a cross-linked mixture of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC). D1 suggests that any known cross-linking agent may be used, including epichlorohydrin, formaldehyde, carbodiimides, and divinylsulphone. An example in D1 describes the use of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) as a cross-linking agent in the presence of citric acid at pH 4.0, with the resulting gel being washed and dried by phase inversion. The polymer of D1 is intended to improve the water-retaining capacity of soil.

Document D2 describes soft absorbent products, such as baby diapers, containing an absorbent core made of polyacrylic superabsorbent polymers and cellulosic fibres, like cotton fibres. D2 aims to improve the perceived softness of these products compared to existing commercial products. The manufacturing process involves mixing fibres and SAP granules in an air stream and then laminating the core between outer layers.

There is a need for superabsorbent polymers that are biodegradable and also impart desirable properties, such as high absorption capacity, good liquid retention, and improved comfort (e.g., softness), when used in absorbent products for personal hygiene. The present invention addresses this need by providing novel biodegradable SAPs based on CMCNa and HEC cross-linked with a carbodiimide, a method for their preparation, and absorbent products incorporating these SAPs, which exhibit surprisingly good softness characteristics.

Summary of the Invention

The present invention provides a biodegradable superabsorbent polymer, a method for its preparation, and an absorbent product incorporating this polymer, which offers environmental benefits and enhanced performance characteristics, particularly in terms of softness when combined with cellulosic fibres.

According to a first aspect, the invention provides an absorbent product comprising a liquid-impermeable first layer, a non-woven second layer, and an absorbent core situated between said first and second layers. The absorbent core comprises cellulosic fibres and a biodegradable superabsorbent polymer. The biodegradable superabsorbent polymer, in turn, comprises sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) cross-linked with a carbodiimide cross-linking agent, wherein said superabsorbent polymer has a degree of cross-linking from 2% to 10% as measured according to Italian Standard ITNA0011 (1990). It has been surprisingly found that this specific combination results in absorbent products with exceptionally high perceived softness.

According to a second aspect, the invention provides a biodegradable superabsorbent polymer comprising sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) cross-linked with a carbodiimide cross-linking agent. This polymer is characterized in that it has a degree of cross-linking from 2% to 10% as measured according to Italian Standard ITNA0011 (1990), an absorption capacity of at least 25 g H_2O per g of polymer, a water retention of at least 60% when measured after absorbing 20 g of deionised water into 1 g of polymer and then drying in a flow of dry air at 30∘C for 3 hours (similar to D1 water release test but applicant specifies retention value), and a shear modulus of at least 2 MPa, measured according to US-A-3 000 000. These properties make it particularly suitable for use in absorbent products.

According to a third aspect, the invention provides a method for preparing a biodegradable superabsorbent polymer. The method comprises the steps of:
(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, wherein the sum of the concentrations of CMCNa and HEC in the aqueous solution is from 3 to 10 wt.%, the concentration of carbodiimide in the solution is from 5 to 15 wt.%, and the pH of the solution during reaction is from 3 to 6;
(ii) washing the gel; and
(iii) drying the gel;
characterized in that the resulting superabsorbent polymer has a degree of cross-linking from 2% to 10% as measured according to Italian Standard ITNA0011 (1990).

The superabsorbent polymers of the invention are biodegradable and exhibit excellent absorption and retention properties, making them suitable replacements for conventional non-biodegradable polyacrylic SAPs. Furthermore, their use in absorbent products containing cellulosic fibres leads to a remarkable improvement in perceived softness.

Detailed Description of the Invention

Biodegradable Superabsorbent Polymer
The biodegradable superabsorbent polymer of the invention comprises sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) cross-linked with a carbodiimide cross-linking agent. Carbodiimides are understood to induce the formation of ester bonds between CMCNa and HEC, and are themselves transformed into urea derivatives during the reaction, leaving no trace of carbodiimide in the final product. A particularly preferred carbodiimide is 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC).
The weight ratio of CMCNa to HEC in the polymer is generally from 0.5 to 5.0, preferably from 0.6 to 3.2. As shown in Example 1 of the invention report, polymers within this preferred ratio range exhibit excellent properties. For instance, ratios from 0.6 to 3.2 provide an absorption capacity of at least 32 g H_2O/g polymer, water retention of at least 60%, and a shear modulus of at least 2.4 MPa.

A key characteristic of the superabsorbent polymer of the invention is its degree of cross-linking, which is from 2% to 10%, as measured according to Italian Standard ITNA0011 published in 1990. This degree of cross-linking is essential for achieving a useful superabsorbent polymer with the desired balance of properties.

The superabsorbent polymer exhibits an absorption capacity of at least 25 g H_2O per g of polymer, preferably higher, for example, as shown in Table 1 of the invention report where values range from 32 to 73 g H_2O/g. It also demonstrates a water retention of at least 60%, with typical values shown in Table 1 ranging from 60% to 77%. The shear modulus, indicating the mechanical strength of the granules, is at least 2 MPa, with typical values in Table 1 ranging from 2.4 to 3.3 MPa. The polymer is typically obtained as white granules.

Method for Preparing the Biodegradable Superabsorbent Polymer
The method for preparing the biodegradable superabsorbent polymer involves the following steps:
(i) Reacting an aqueous solution of CMCNa and HEC with a carbodiimide cross-linking agent in the presence of an acid catalyst to produce a polymer gel.
* 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.%. Concentrations outside the 3-10 wt.% range may impede effective cross-linking.
* The weight ratio of CMCNa to HEC is from 0.5 to 5.0, preferably from 0.6 to 3.2.
* The concentration of the carbodiimide cross-linking agent (e.g., EDC) in the solution is from 5 to 15 wt.%, preferably from 5 to 10 wt.%. This concentration range is important for obtaining a gel with good mechanical properties.
* An acid catalyst is used to facilitate the cross-linking reaction. The pH in this step is usually from 3 to 6, preferably from 3.5 to 4.5. Citric acid is a typical acid catalyst, though others can be used.
(ii) Washing the gel. The gel obtained from step (i) is washed, preferably with water, and more preferably with deionised water, as this can result in polymers with higher absorption capacity.

(iii) Drying the gel. The washed gel is then dried. A preferred drying method is phase inversion, for example, by contacting the gel with a liquid that does not dissolve the polymer but absorbs water, such as acetone, until the polymer precipitates as white granules. Drying by phase inversion generally results in a higher absorption capacity compared to air drying. However, air drying may also be used.

This method, utilizing the specified conditions, results in a superabsorbent polymer having a degree of cross-linking from 2% to 10%.

Absorbent Product
The invention also pertains to an absorbent product designed to absorb bodily fluids. Examples include baby diapers, adult incontinence items, female hygiene products, and bandages. Such products typically comprise a liquid-impermeable first layer (e.g., a polyethylene backsheet), a liquid-permeable second layer made from a non-woven material (e.g., a polypropylene topsheet), and an absorbent core positioned between these two layers. The absorbent core comprises the biodegradable superabsorbent polymer of the invention, as described above, and cellulosic fibres. Examples of suitable cellulosic fibres include cotton, flax, and rayon fibres. The absorbent core may contain, for example, about 30 wt.% of the superabsorbent polymer, with the remainder being fibres, though other compositions are possible. While it is possible to use the superabsorbent polymer on its own in the core, it is generally preferred to mix it with fibres.

A significant and surprising advantage of using the claimed biodegradable SAPs in combination with cellulosic fibres is the greatly enhanced perceived softness of the absorbent product. As demonstrated in Example 2 of the invention report (Table 2), absorbent products made with CMCNa/HEC SAPs of the invention and cotton fibres exhibited perceived softness values of 72 and 80, whereas a similar product made with a conventional polyacrylic SAP (Superwet A1000) had a perceived softness of only 31. This improvement in softness was observed with various cellulosic fibres, including flax and rayon. In contrast, when synthetic fibres (polypropylene or polyamide) were used instead of cellulosic fibres, the perceived softness for products made with either the inventive SAPs or the polyacrylic SAP was very similar. This indicates a specific synergistic interaction between the claimed biodegradable SAPs and cellulosic fibres that leads to unexpected softness.

The absorbent products can be manufactured using conventional methods. For example, the absorbent core can be formed by conveying the fibres in a stream of hot air to a rotating vacuum drum, feeding the SAP granules into the stream of fibres to achieve mixing, and then laminating the formed core between the first and second layers.

Examples

The invention is further illustrated by the following non-limiting examples, derived from the applicant's invention report.

Example 1: Preparation and Properties of CMCNa/HEC Superabsorbent Polymers

A series of superabsorbent polymers were prepared as follows: An aqueous solution containing CMCNa and HEC was prepared with the sum of their concentrations at 5 wt.%. The weight ratio of CMCNa to HEC was varied as indicated in Table 1 below.

1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) was added as a cross-linking agent to a concentration of 7 wt.% in the aqueous solution. Citric acid was added as a catalyst, resulting in a solution pH of 4.0. The gel obtained was washed with deionised water and dried by phase inversion in acetone until white granules precipitated. All prepared CMCNa/HEC polymers had a degree of cross-linking of 5% as measured by Italian Standard ITNA0011 (1990).

The absorption capacity, water retention, and shear modulus were measured according to US-A-3 000 000. Acceptable products require an absorption capacity of at least 25 g H2O/g polymer, a water retention of at least 60%, and a shear modulus of at least 2 MPa. Properties of a commercial polyacrylic SAP (Superwet A1000) were: absorption capacity 45 g H2O/g, water retention 65%, shear modulus 3.0 MPa.

The results for the prepared CMCNa/HEC SAPs are shown in Table 1:

Table 1: Properties of CMCNa/HEC Superabsorbent Polymers

Sample Number	CMCNa to HEC wt. Ratio	Absorption Capacity (g H2O 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

All CMCNa/HEC superabsorbent polymers listed in Table 1 exhibit excellent properties and meet the acceptance criteria.

Example 2: Absorbent Product Performance
Absorbent products were prepared using CMCNa/HEC SAPs (Sample 4 and Sample 11 from Example 1) and Superwet A1000 (polyacrylic SAP). A stream of cotton fibres in hot air was fed into a rotating vacuum drum, SAP granules were fed into the stream, and the resulting absorbent core (containing 30 wt.% SAP) was laminated between a liquid-impermeable first layer and a non-woven second layer. Absorption capacity and water retention were measured as per US-A-3 000 000. Perceived softness was evaluated by a test panel on a scale of 1-100 (higher is better).
Results are shown in Table 2:

Table 2: Absorbent Product Properties

Superabsorbent polymer used	**CMCNa/HEC (Sample 4)**	**CMCNa/HEC (Sample 11)**	**Polyacrylic (Superwet A1000)**
Absorption Capacity (g H2O per g polymer)	65	95	80
Perceived Softness	80	72	31
Water retention (%)	65	70	72

The results clearly demonstrate the superior perceived softness of absorbent products made with the inventive CMCNa/HEC SAPs and cotton fibres compared to a product with a conventional polyacrylic SAP. Similar results for softness were obtained when cotton fibres were replaced by other cellulosic fibres (flax, rayon).

Claims

1. An absorbent product comprising:
   a. a liquid-impermeable first layer;
   b. a non-woven second layer; and
   c. an absorbent core between said first layer and said second layer, the absorbent core comprising:
   i. cellulosic fibres; and
   ii. a biodegradable superabsorbent polymer comprising sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) cross-linked

with a carbodiimide cross-linking agent,
characterized in that said biodegradable superabsorbent polymer has a degree of cross-linking from 2% to 10% as measured according to Italian Standard ITNA0011 (1990).

2. The absorbent product according to claim 1, wherein the weight ratio of CMCNa to HEC in the biodegradable superabsorbent polymer is from 0.6 to 3.2.

3. The absorbent product according to claim 1 or 2, wherein the carbodiimide cross-linking agent is 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC).

4. The absorbent product according to any preceding claim, wherein the cellulosic fibres are selected from the group consisting of cotton fibres, flax fibres, and rayon fibres.

5. The absorbent product according to any preceding claim, wherein the biodegradable superabsorbent polymer is in the form of granules and constitutes from 15 wt.% to 50 wt.% of the absorbent core, for example 30 wt.%.

6. The absorbent product according to any preceding claim, wherein the product exhibits a perceived softness value of at least 70 on a scale of 1 to 100 when the absorbent core contains cotton fibres and approximately 30 wt.% of the biodegradable superabsorbent polymer.

7. A biodegradable superabsorbent polymer comprising sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) cross-linked with a carbodiimide cross-linking agent, characterized in that the polymer has:
   a. a degree of cross-linking from 2% to 10% as measured according to Italian Standard ITNA0011 (1990);
   b. an absorption capacity of at least 25 g H_2O per g of polymer as measured according to US-A-3 000 000;
   c. a water retention of at least 60%; and
   d. a shear modulus of at least 2 MPa as measured according to US-A-3 000 000.

8. The biodegradable superabsorbent polymer according to claim 7, wherein the weight ratio of CMCNa to HEC is from 0.6 to 3.2.

9. The biodegradable superabsorbent polymer according to claim 7 or 8, wherein the carbodiimide cross-linking agent is 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC).

10. The biodegradable superabsorbent polymer according to any one of claims 7 to 9, wherein the polymer is in the form of white granules.

11. A method for preparing a biodegradable superabsorbent polymer as defined in any one of claims 7 to 10, the method comprising the steps of:
    a. 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, wherein:
    i. the sum of the concentrations of CMCNa and HEC in the aqueous solution is from 3 to 10 wt.%;
    ii. the concentration of the carbodiimide cross-linking agent in the aqueous solution is from 5 to 15 wt.%; and
    iii.the pH of the aqueous solution during the reaction is from 3 to 6;
    b. washing the polymer gel with water; and
    c. drying the washed polymer gel;
    wherein the resulting superabsorbent polymer has a degree of cross-linking from 2% to 10% as measured according to Italian Standard ITNA0011 (1990).
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 claim 11 or 12, wherein the concentration of the carbodiimide cross-linking agent is from 5 to 10 wt.%.

14. The method according to any one of claims 11 to 13, wherein the pH of the aqueous solution during the reaction is from 3.5 to 4.5, and the acid catalyst is citric acid.

15. The method according to any one of claims 11 to 14, wherein the polymer gel is washed with deionised water and dried by phase inversion, optionally using acetone.