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SCIENTIFIC PAPER

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SUPER SLURPERS FROM RENEWABLE RESOURCES: SYNTHESIS, PROPERTIES, APPLICATIONS

The aim of the following investigation was the replacement of super slurpers on the basis of neutralized crosslinked polycrylic acid (PANC) by those on the basis of renewable resources. It has been demonstrated, that starch is the best base material for the synthesis of super slurpers with respect to practicality and price. The starch is derivatized and crosslinked with different agents to exhibit high absorption capacities. Measurement techniques of the different absorption capacities, kinetic properties of the absorption process, toxicological properties, biochemical decomposition, compostability and the different applications are discussed.

Super slurpers (super absorbents) are materials which exhibit outstanding absorption power for liquids, 20 to several 100 fold of its own volume, and which do not release the liquid on mechanical the stress. The liquids may be salt containing aqueous solutions, organic liquids and their mixtures. In case of aqueous solutions super slurpers consist of crosslinked polymers with ionic and/or polar functional groups. Since 1970 powerful super slurpers, which can be used for several applications have been developed on the basis of neutralized crosslinked poly(acrylic acid) (PANC).

This paper presents the synthesis of super slurpers from polysaccharides, selected properties and applications [1, 2, 3].

SYNTHESIS

Base materials for the synthesis of super slurpers may be polysaccharides such as cellulose, starch, and pectins. Cellulose is obtained from wood. Starch is mainly produced from indian corn, potatoes, and cereals, but also from pea, guar, locust bean, tapioca, etc. Pectin is obtained from the cell wall of plants.

Concerning the marketability of super slurpers, the price of raw materials and, therefore, the price of super slurpers is essential. Commercial starch costs 0.3 to 0.5 $ per kilogram. Comparing this price with the price of a conventional super slurper (poly(acrylic acid), neutralized, crosslinked, PANC) of 2 to 2.5 $ per kilogram it seems realistic to be able to produce super slurpers from starch within the price window of conventional super slurpers.

The synthesis of super slurpers from polysaccharides requires chemical modification of the polysaccharides.

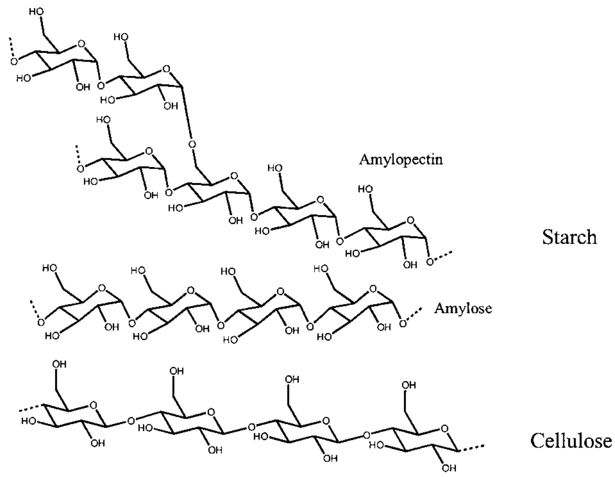

Figure 1. Structures of cellulose und starch

Because of the cheapness of the raw material and the good handling of starch, this may be the best raw material. Figure 1 demonstrates the structures of starch and cellulose. Starch consists of the two components amylopectin and amylose.

The first step of the chemical modification is derivatization; that means the introduction of ionic or polar groups into the starch molecule. In principle there are several possibilities for this step: oxidation, esterification, etherification, phosphatizaton. As a good catalyst for selective oxidation of the starch molecule without bond cleaving has not yet been found, esterification with native acids or etherification would be the best possibilities. Figure 2 demonstrates some principal possibilities for the derivatization of starch.

In nature this derivatization can also be found: Pectin (cell wall of plants) and carageenan (Irish moss, Irish gum) are natural products which contain ionic groups (see Figure 3). They are too expensive as raw materials for the production of super slurpers.

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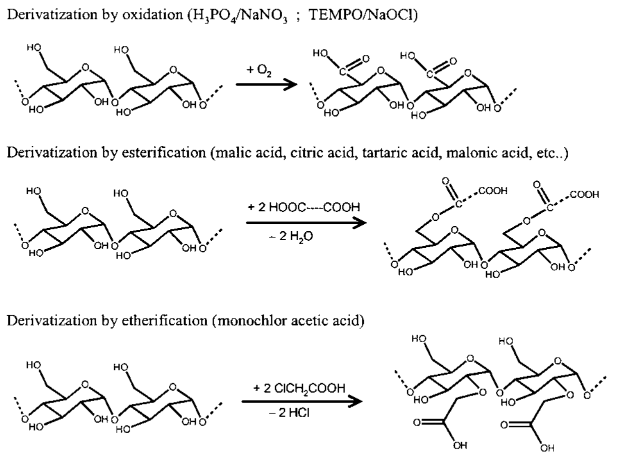

Figure 2. Derivatization of starch (TEMPO = 2,2,6,6–Tetramethyl–1–piperidinoxyl)

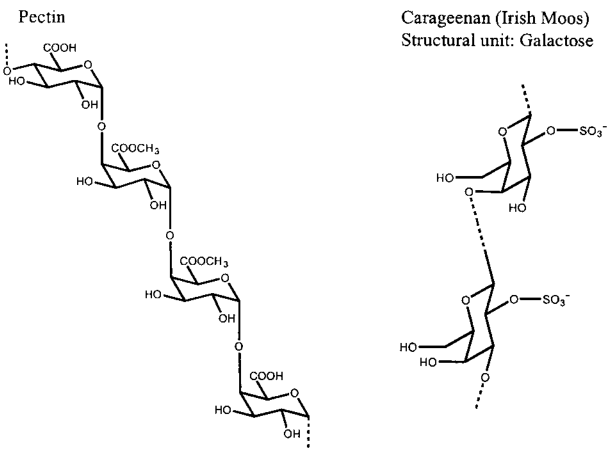

Figure 3. Structures of pectin und carageenan

The second step of the chemical modification is the crosslinking of the derivatized starch. This may be done with crosslinking agents (i.e. citric acid) or intermolecularly with the existing functional groups of the derivatized starch. Figures 4 and 5 demonstrate the two described possibilities with an etherized starch, carboxymethyl starch.

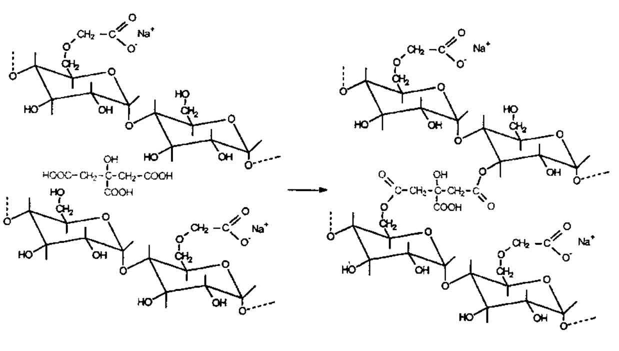

Figure 4. Crosslinking of carboxymethyl starch (CMS) with citric acid

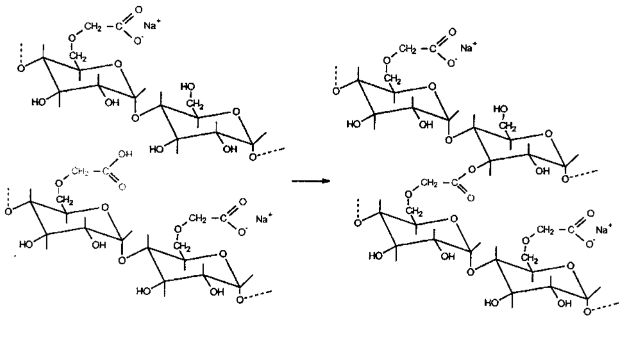

Figure 5. Intermolecular crosslinking of carboxymethyl starch (CMS)

Regarding the crosslinking agents it seems valid to use non–toxic substances, i.e. natural multifunctional acids. Super slurpers from renewable resources can then also be used as medical products (products for the pharmaceutical industry) and as food additives.

PROPERTIES

Figures 6 and 7 demonstrate the absorption of aqueous salt containing liquids into a super slurper. The water molecules penetrate together with the salt molecules into the unswollen gel resulting in a swollen gel. Additionally, Figure 7 shows that the sorption capacity is substantially reduced by electrolytes. This could be explained by the effect that the influence of the ionic and polar groups of the super slurper would be partly inhibited by the salt molecules. This effect also appears with conventional super slurpers from crosslinked poly(acrylic acid).

Three essential properties of super slurpers will be demonstrated: a) the sorption capacity under different conditions, b) the toxic properties, and c) the environmental compatibility.

Normally the sorption capacity would be measured as the swelling degree $q = m_{LM}/m_{Abs}$ in sodium chloride solution (C = 9 g/L) with m_{LM} = mass of the sodium

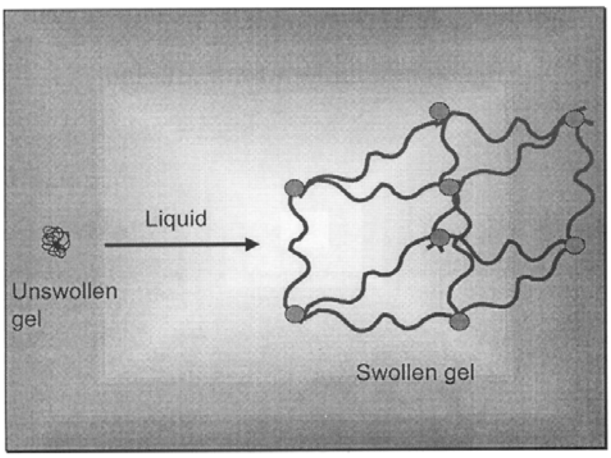

Figure 6. Swelling of a super slurper

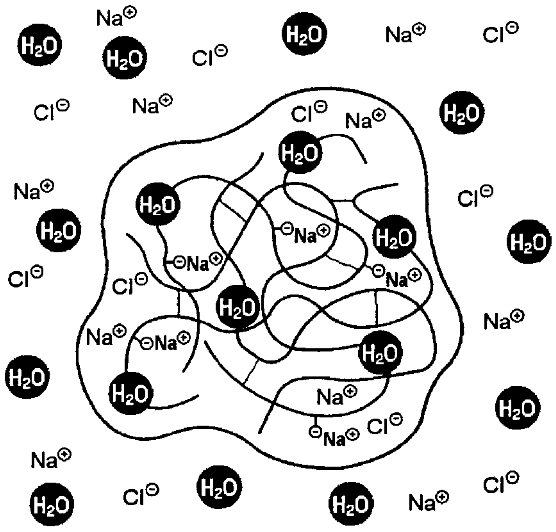

Figure 7. Swollen gel with outside NaCl–solution and Na^{+} – and Cl^{-} –ions penetrated into the gel

chloride solution and m_{Abs} = mass of the absorber. The swelling time is one hour. The sodium chloride solution replaces urine.

Regarding the sorption capacity there are three different generally accepted properties which are measured by distinct accepted procedures:

1) The free swelling capacity q_{FSC}; swelling time = 1 hour.

2) The absorption under load q_{AUL}; swelling time = 1 hour. The swelling degree is measured under a load of 460 kg/m^2 (this corresponds to a pressure of 4500 Pa). The apparatus for the measurement of q_{AUL} is seen in Figure 8.

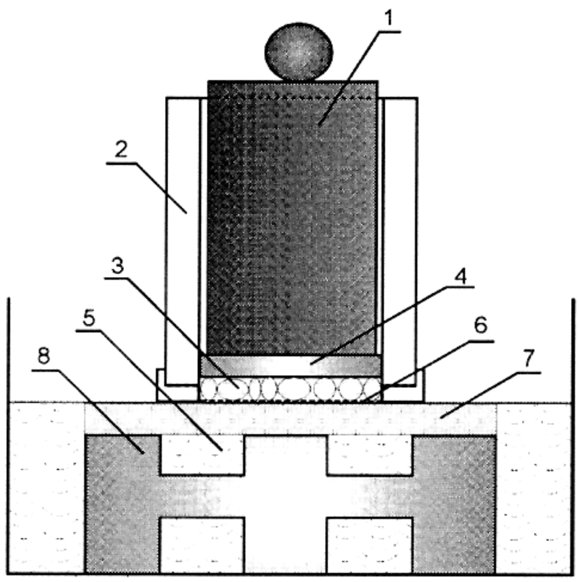

Figure 8. Apparatus for the measurement of absorption under load (AUL)
1. Weight, 2. Cylinder, 3. Absorber, 4. Teflon disc, 5. Test solution, 6. Metal network, 7. Filter plate, 8. Base

3) The centrifuge retention capacity q_{CRC}; swelling time before centrifugation: 1 hour. The swelling degree is measured after treatment of the swollen gel in a centrifuge (diameter = 24 cm, duration of the centrifugation = 2 minutes, rotor speed = 2800 min^{-1}).

Table 1 compares the sorption capacities of super slurpers based on poly(acrylic acid) (PANC) and carboxymethyl starch (CMSC) of the 1st and 2nd generation. The definition 1st and 2nd generation means degrees of development; the 2nd generation represents a higher degree of development. The sorption capacities of CMSC, 2nd generation, achieve approximately 70 % of the sorption capacities of PANC. It seems realistic to optimize CMSC to higher sorption capacities through further research and development in this area.

Table 1. Capacities of super slurpers.
Swelling degrees $q = m_{LM}/m_{Abs}$ in sodium chloride solution (C = 9 g/L) m_{LM} = Mass of the sodium chloride solution; m_{Abs} = Mass of the absorber

Super slurper	q_{FSC} [g/g]	q_{AUL} [g/g]	q_{CRC} [g/g]
PANC	40 – 54	20 – 30	30 – 40
CMSC 1st generation	20 – 30	10 – 15	10 – 20
CMSC 2nd generation	35 – 40	15 – 20	25 – 30

Figure 9 demonstrates a scanning electron microscope recording of crosslinked carboxy–methyl starch.

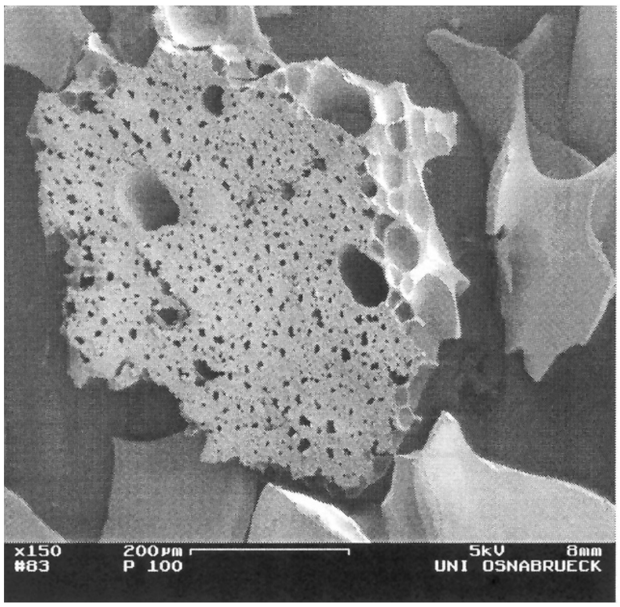

Figure 9. Scanning electron microscope recording of crosslinked carboxymethyl starch (CMSC)

For the rapid penetration of liquids, super slurpers should have a diameter from 100 to 500 μm and, additionally, they should have a porous structure. For crosslinked carboxymethyl starch this is achieved by a patentable procedure. The electron microscope recording shows the porous structure of CMSC.

Table 2 compares the toxicological properties of crosslinked carboxymethyl starch and crosslinked poly(acrylic acid). Carboxymethyl starch has been approved as a medical product (i.e. pharmaceutical product). In several countries CMS has been approved as a food additive.

Table 2. Toxicological properties of carboxymethyl starch, crosslinked (CMSC) and poly(acrylic acid), neutralized, crosslinked (PANC)

Carboxymethyl starch, crosslinked (CMSC)

- No carcinogenic effect known, anticarcinogenic effect. 50% inhibition on tumor growth with respect to distinct tumors.

- No irritating effect on the skin (HET–CAM–Test)

Poly(acrylic acid), neutralized, crosslinked (PANC)

- Nachrichten aus der Chemie, **47**(1999) Nr. 9, Seite 1119 Official journal of the Gesellschaft Deutscher Chemiker (GDCh):
  "*Carcinogenic materials, category 4 (materials with threshhold effect): neutralized, crosslinked Poly(acrylic acid) ("Super shurper"), ...*

- MAK – und BAT–Werte–Liste 2000
  Senatskommision zur Prüfung gesundheitsschäd- licher Arbeitsstoffe der Deutschen Forschungs-gemeinschaft.
  "*Poly(acrylic acid) (neutralized, crosslinked), carcinogenic, category 4*"

Table 3 compares the biochemical decomposition and compostability. In contrast to poly(acrylic acid), carboxymethyl starch does not consist of a pure carbon chain; therefore CMSC should exhibit good biochemical decomposition and good compostability. This has been verified by experiments. Therefore, it would be possible to compost CMSC in appropriate plants; the evolved carbon dioxide has been received from the raw material delivering vegetable by photosynthesis. In contrast to petrochemical products such as PANC, no additional carbon dioxide is produced with respect to CMSC. The application of CMSC is carbon dioxide neutral.

Table 3. Biochemical decomposition und compostability.

Biochemical decomposition

	COD [mg/g]	BOD_5 [mg/g]	$\beta = BOD_5/COD$	
Starch	1100	680	62	good decomposition
CMSC	860	280	38	good decomposition
PANC	880	70	8	bad decomposition

COD = chemical oxygen demand
BOD_5 = biological oxygen demand after 5 days

Decomposition in compost

	20 days	90 days
Celluloze	57%	80%
CMSC	38%	50%
PANC	–	14% (max.)

APPLICATIONS

Super slurpers from renewable resources can be used for the following applications:

- Diapers, Napkins
- Incontinence articles
- Hygienic products
- Ultrasonic gels
- Electrode gels
- Diet food (thickening material)
- Wound plaster for wet wounds
- Humidity protection for food packings
- Water storage for plants in dry areas or cities
- Flocculating agents
- Sewage sludge dehydration
- Ion exchanger

The developments for diapers and ultrasonic gels are ready for use. The other applications could be realized in the near future.

The replacement of conventional super slurpers (PANC) by those from renewable resources requires more activities from manufacturers, fabricators, consumers, and politicians concerning sustainable concepts.

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REFERENCES

[1] M.D. Lechner, W. Lazik, "Vernetzte Polysaccharid–Derivate als Superabsorber aus nachwachsenden Rohstoffen als biologisch abbaubarer Synthetika–Ersatz mit umweltgerechter Entsorgungsmöglichkeit und ihre physikalisch–

chemischen Eigenschaften in wäßrigen Systemen.", Deutsche Bundesstiftung Umwelt, Az.: 05951, 1998

[2] M.D. Lechner, W. Lazik, "Optimierung der Festphasenreaktionen zur Herstellung von Absorbermaterialien aus Stärkeprodukten und deren wissenschaftliche Untersuchung der resultierenden Struktur–Eigenschafts–Beziehungen.", Fachagentur Nachwachsende Rohstoffe, FKZ.: 96 NR080–F, 2000

[3] M.D. Lechner, W. Lazik, Offenlegungsschrift DE 196 54 745 A 1, "Biologisch abbaubares Absorptionsmittel"

IZVOD

SUPER APSORBENTI NA BAZI OBNAVLJAJUĆIH SIROVINA: SINTEZA, SVOJSTVA, PRIMENA

(Naučni rad)

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Cilj sledećeg istraživanja je bio zamena super apsorbenata na bazi neutralizovane umrežene poli(akrilne kiseline) (PANC) super apsorbentima na bazi obnavljajućih sirovina. Pokazano je da je u pogledu praktičnosti i cene skrob najbolji osnovni materijal za sintezu super apsorbenata. Pravljeni su različiti derivati skroba i umrežavan je različitim sredstvima u cilju postizanja velike moći apsorpcije. Diskutovane su različite tehnike merenja apsorpcione moći, kinetičkih svojstava apsorpcionog procesa, toksikoloških svojstava, biohemijske razgradnje, kao i različite primene super apsorbenata.

Ključne reči: Superapsorbent • Obnavljajuće sirovine • Polisaharidi • Ultrasonični gel •
Key words: Super slurpers • Renewable resources • Polysaccharides • Diapers • Ultrasonic gels •