

Association of Cereal Research (AGF)

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In cooperation with

Max Rubner-Institute
Institute of Safety and Quality of Cereal

65th Starch Convention

April 09th – 10th 2014

Detmold, Germany

Program

Evening Program

Exhibition

Participants

Summaries



Wednesday, April 09th 2014

13³⁰ **Opening Remarks** by the President of the Association of Cereal Research, **Götz Kröner**, Ibbenbüren (Germany)

13⁴⁵ **Saare-Medal Awards Ceremony** for Dr. Eric Bertoft, Guelph (Canada)

1. Plenary Lecture

- 1.1. **Wolfgang Bergthaller**, Lage (Germany)
1949-2014: Starch Conventions from past to present

2. Starch Biosynthesis and Structure

- 2.1. **Eric Bertoft**, Guelph (Canada)
Secondary effects of starch branching patterns in plants with starch synthase (ss-) mutations
- 2.2. **Serge Perez**, Grenoble (France)
Starch@Synchrotron
- 2.3. **Katja Loos**, AG Groningen (The Netherlands)
Physical properties and structure of enzymatically synthesized amylopectin analogs

16⁰⁰ Coffee Break

- 2.4. **Chi-Wah Yeung** und **Hubert Rein** Bonn (Germany)
Assay of surface energy of starch
- 2.5. **Marcela Slukova**, Prague 6 (Czech Republic)
The effect of bakery improvers on staling of wheat bakery products

3. Modification

- 3.1. **Mohammad Naushad Emmambux**, Pretoria (South Africa)
Starch modification with stearic acid for 'clean' label starches
- 3.2. **Oluwatoyin A. Odeku**, Ibadan (Nigeria) and **Katharina M. Picker-Freyer**, Halle/Saale (Germany)
Natural and modified yam starches as directly compressible excipients in tablet formulation

18⁰⁰ Exhibitor's Forum - short term presentations

Thursday, April 10th 2014

08³⁰

3. Modification

- 3.3. **Christina Gabriel, Henning Winkler, Rainer Rihm, Waltraud Vorweg** Potsdam (Germany)
Optimized starch esters for materials
- 3.4. **Andreas Blennow**, Frederiksberg C (Denmark)
Clean modification of starch using a semi-solid-state branching enzyme-assisted protocol
- 3.5. **Hanna Staroszczyk**, Gdansk (Poland)
Rheology of potato starch chemically modified with microwave-assisted reactions

10⁰⁰ Coffee Break

To be continued on page before last

Evening Program

Wednesday, April 09th 2014

After the Exhibitor's Forum "**Bread and Wine**"-Get-together in the "Haus des Brotes" (Exhibition Hall).

Wine

Baden

2011er Kirchberghof, Weingut Dr. Benz
Spätburgunder Rotwein, trocken

Franconia

2012er Weingut Roth
Domina Qualitätswein, trocken

Palatinate

2012er Dürkheimer Riesling
Qualitätswein, trocken

Rhinehessen

2012er Rivaner Kabinett
Prädikatswein, trocken

Wuerttemberg

2012er Schlossgut Hohenbeilstein
Lemberger, rosé, trocken



Bread

Savoury snacks

Pretzels

With compliments

vandemoortele

20⁰⁰ **Social gathering** at Strates Brauhaus, Lange Straße 35, Detmold

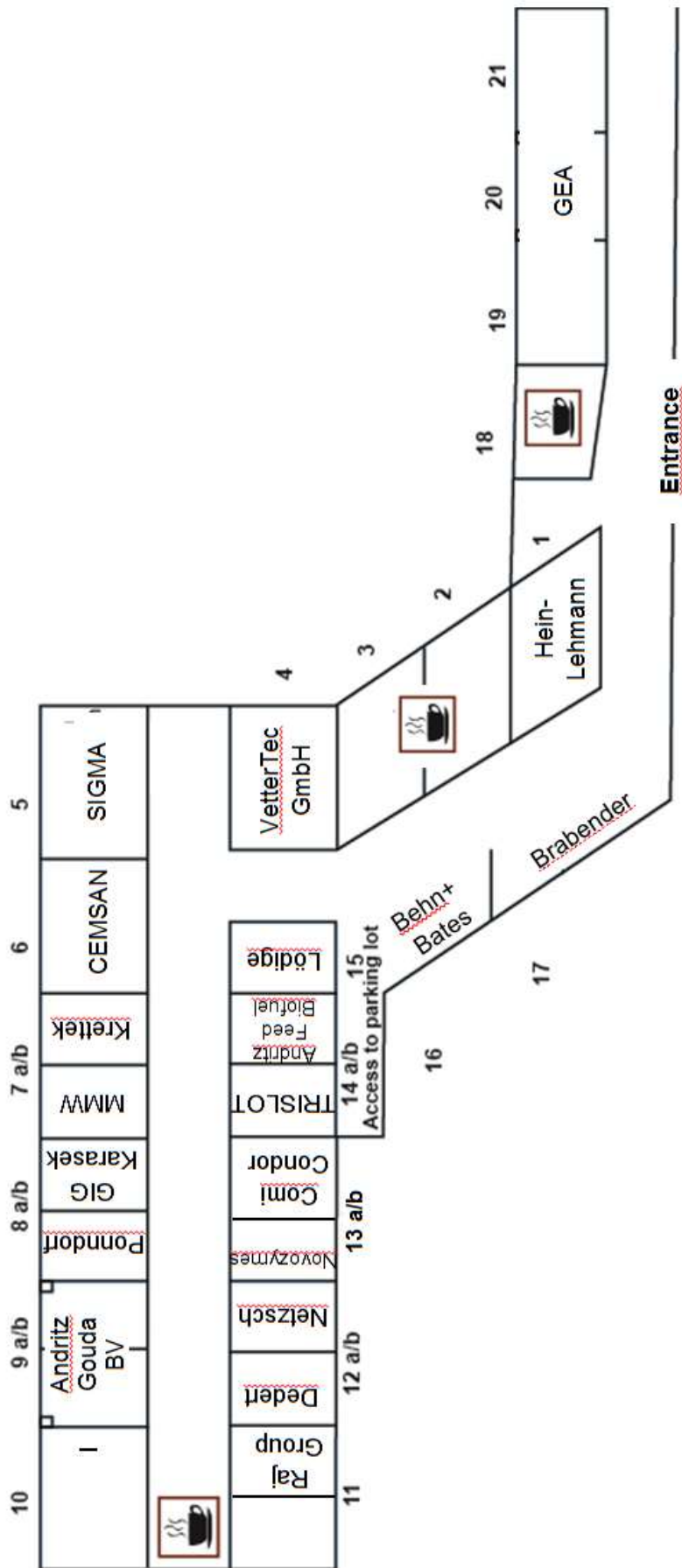
Please make your reservation until 4pm, if possible.

Thank you!

Exhibition

Exhibition Hall Association of Cereal Research Stand allocation

10th European Bioethanol and Bioconversion Technology Meeting
and 65th Starch Convention from April 8th – 10th 2014



Exhibition

Andritz Feed & Biofuel Div., Cumming, GA 30040 (USA)

Andritz Gouda BV, PD Waddinxveen (Netherland)

Behn & Bates Maschinenfabrik GmbH & Co. KG, Münster (Germany)

Brabender GmbH & Co.KG, Duisburg (Germany)

Cemsan A.S., Arifiye, Sakarya (Turkey)

Comi Condor SPA, Santa Christina E Bissone (Italy)

GEA Westfalia Separator Group GmbH, Oelde (Germany)

Gebr. Lödige Maschinenbau GmbH, Paderborn (Germany)

GIG Karasek GmbH, Gloggnitz (Austria)

HEIN, LEHMANN GmbH, Krefeld (Germany)

Krettek Filtrationstechnik GmbH, Viersen (Germany)

MMW Technologie GmbH, Lutherstadt Wittenberg (Germany)

Netzsch Pumpen & Systeme GmbH, Waldkraiburg (Germany)

Novozymes Deutschland GmbH, Bad Kreuznach (Germany)

Ponndorf Anlagenbau GmbH, Kassel (Germany)

RAJ PROCESS EQUIPMENTS & SYSTEMS PVT. LTD.,
Akurdi, Pune (India)

Sigma Process Technologies, Atasehir/Istanbul (Turkey)

Trislot N.V., Waregem (Belgium)

VetterTec GmbH, Kassel (Germany)

W. Kunz dryTec AG Swiss Combi / Dedert Corporation,
Homewood (Schweiz)

Exhibition

Exhibitor's Forum – Short Presentations (Wednesday, April 09th, approx. 6.00 p.m.)

- 1. Gerhard Ruland**, Netzsch Pumpen & Systeme GmbH (Germany)
Lifetime optimization of positive displacement pumps and sealing concepts
- 2. Thomas Strandt**, MMW Technologie GmbH (Germany)
MMW Dry Milling Techniques for Wheat Starch and Bioproducts
- 3. Petra Salzmann**, Novozymes Deutschland GmbH (Germany)
Innovative enzymatic solutions from Novozymes for grain processing

Participants

Effective April 03rd 2014

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Summaries

1. Plenary Lecture

- 1.1. **Wolfgang Bergthaller**, Lage (Germany)
1949-2014: Starch Conventions from past to present

In 2014 the Association for Cereal Research celebrates with a number of 65 successive conferences an extraordinary success in this highly specified scientific field. The registration of about 16 800 participants from home and abroad confirms the importance of the Starch Conventions. A sum of approximately 1500 lectures dealing with fundamental aspects (biosynthesis, granule architecture, crop production, isolation), modification, application, saccharification, and renewable resources could attract an obviously always interested auditory.



Austrian by birth (born 1942 in Salzburg) I received the academic education at the University of Natural Sciences in Vienna. I finalized studies in fermentation and biotechnology as engineer in food technology in June 1967. In 1968 I joined the Federal Centre for Cereal Processing in Detmold and became research employee in its starch division. Until retirement in 2006 the career as official led finally to a position as deputy head of the Institute of Starch and Potato Processing.

2. Starch Biosynthesis and Structure

- 2.1. **Eric Bertoft** and **Koushik Seetharaman**, St Paul (USA),
Fan Zhu, Auckland (New Zealand)
Secondary effects of starch branching patterns in plants with starch synthase (ss-) mutations

There are generally two major types of starch synthases involved in the elongation of the glucosyl chains in the starch components during biosynthesis. Granule-bound starch synthase (GBSS) is responsible for the synthesis of amylose, whereas starch synthase (SS), formerly often called "soluble starch synthase", elongates the chains of amylopectin. SS consists, in fact, of several types of enzymes: in a simplified context, SS1 synthesizes the shortest chains with a degree of polymerization (DP) ≤ 10 , SS2 elongates the short chains into DP approximately 12–24, SS3 synthesizes longer chains of DP > 30 , and SS4 is involved in the initiation of starch granules. The absence of one or more of these enzymes, due to ss- mutations, results therefore in altered chain profiles in the starch [1]. Surprisingly, however, not only the chain lengths are affected, but also the distribution of the branches in the amylopectin appears to be different from non-mutant starch. This is most probably due to the fact that the enzymes form complexes with other enzymes involved in starch biosynthesis, such as the branching enzymes [2]. In the absence of one or more SSs, novel complexes are formed [3], which results in secondary effects on the structure of the starch components. This work examined the structure of amylose and the branching pattern of the clusters in amylopectin from endosperm starch in the ss3- mutation of maize (du1) and barley (amo1), as well as the effect of diverse single (ss1-, ss2-, ss3-) and double ss-mutations (ss1-ss2- and ss1-ss3-) on the transient starch in leaves of Arabidopsis.

The starch samples were debranched and analyzed by gel-permeation chromatography on Sepharose CL 6B. All ss-mutations in Arabidopsis resulted in higher amylose concentration in the starch compared to the wild type (WT) plant. The same was found for the du1 mutant maize starch. It was also found that the composition of amylose

chains altered, so that, generally, the ratio of long to short amylose chains increased due to a proportionally higher increase of long chains compared to short chains. The only exception to the rule was the double mutant *ss1-ss2-* of Arabidopsis, in which the ratio of long to short chains was similar to that in the WT. Therefore, albeit the SS enzymes are involved in the elongation of amylopectin chains and only GBSS is known to be active in amylose synthesis, it appears that SSs indirectly also affects the synthesis, as well as the structure, of amylose.

The unit chain profiles of the amylopectin component in maize and barley starches were analyzed by high-performance anion-exchange chromatography. In both plants, the relative number of long chains was reduced and the number of short chains increased in the SS3 deficient plants (*du1* and *amo1*, respectively). The same was found for the internal unit chains, i.e. long internal B-chains decreased in number, whereas short internal B-chains increased compared to the non-mutant plants. Therefore, the average chain length of the internal chains decreased in the mutant samples. However, some interesting differences were noted: Whereas both the external chain length (ECL) and the internal chain length (ICL) of the amylopectin decreased in *du1* maize [4], only ICL decreased in *amo1* barley [5]. Thus, the similar SS3 deficiency in these two different plants gave rise to different effects on the structure of the amylopectin component.

To analyze the changes in the branching pattern in SS deficient starches, the clusters were isolated from the amylopectins by partial hydrolysis with the α -amylase of *B. amyloliquefaciens*. The enzyme attacks fast the longer internal chains between clusters ($ICL \geq 9$) in amylopectin. When the clusters, which have $ICL < 9$, have been released, the reaction rate becomes slow and the clusters can be collected and analyzed further for their composition of chains and building blocks [6, 7]. With the exception of the *ss1-ss2*-mutant of Arabidopsis, all *ss*-mutants gave rise to larger clusters with an increased average number of chains (NC) and number of building blocks (NBbl) per cluster. However, large differences were found depending on which SS enzyme was absent and also depending on the type of plant. Thus, in the *ss3-* mutant of Arabidopsis NC increased with 2.2 chains, and this was mostly due to an increase of α -chains (unsubstituted chains), but also of short b_1 -chains (substituted chains). In *du1* maize NC increased with 2.7 chains, which also depended on more α -chains, but in addition the number of long b_2 - and b_3 -chains increased. This suggested differences in the branching pattern of the two SS3 deficient plants, although in both plants the major effect on the building blocks was an increase of the smallest blocks with only two chains (group 2 building blocks). The same mutation in *amo1* barley resulted instead in a significant increase of the number of the large building blocks of groups 4–6, which consist of four or more chains.

The other *ss*-mutations in Arabidopsis also gave rise to different compositions of both the chains and building blocks in the clusters. The strongest effect was found in the double mutant *ss1-ss3-*, in which the size of the clusters increased dramatically from NC of 10.6 to NC 18.3 and the number of large building blocks nearly doubled. In contrast, the clusters in the other double mutant (*ss1-ss2-*) possessed almost identical composition to the clusters in WT. However, this was the only sample in which the average inter-block distance increased significantly from 6.7 to 7.5 glucosyl residues.

It can thus be concluded that any *ss*-mutation affects the structure of both the amylose and the amylopectin component in starch. As SS enzymes have been shown to be involved in the elongation of the chains in amylopectin [8], the changes in amylose structure and in the branching pattern of clusters in amylopectin must be due to pleiotropic effects of the *ss* genes and to altered enzyme complexes that are formed in the absence of one or more enzymes.

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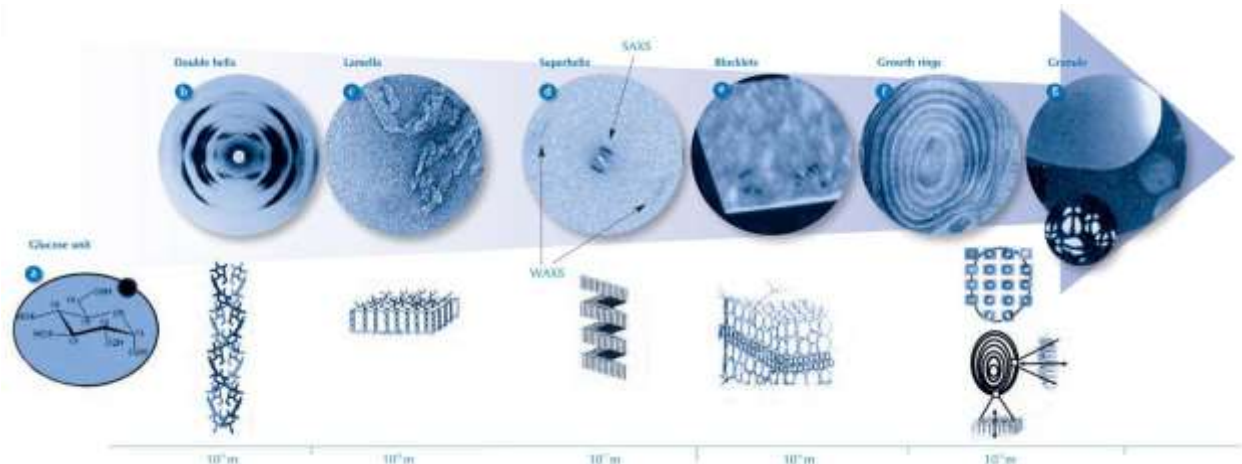
Dr. Eric Bertoft is at present a research fellow at the Department of Food Science and Nutrition at the University of Minnesota, U.S.A., and acts as associate professor at Åbo Akademi University in Finland. His research is mainly focussed on the molecular structure of starch components and their contribution to the granular structure and the properties of starch.

2.2. **Serge Perez**, Grenoble (France) Starch@Synchrotron

Recent developments in methods and instrumentation, using X-ray synchrotron radiations, have contributed to major advances in our understanding of the fine structure of amylose and amylopectin. The structure of the starch granule slowly unravels with new insight into key structural features.

These X-ray results corroborate biochemical studies of the amylopectin molecule which show that this huge molecule is organised in crystalline clusters of double helices. Each lamella, revealed in the X-ray diffraction research, is made up of about 100 double-stranded helices, each consisting of about 20 glucose units. The double helices are very densely packed, with a high degree of regularity, like in a crystal, having a theoretical density of 1.55. This structural arrangement is in agreement with the results derived from biochemical studies. In this model, the branch points (the (1-6) links) in the amylopectin molecules are located in the less organised (or more amorphous) regions between the clusters. Amylose is entangled with amylopectin, but so far nobody knows exactly how. Additional X-ray studies, using the techniques of small-angle and wide angle scattering (SAXS and WAXS) to analyse hydrated starch, show that the lamellae of double helices are probably organised in a helical superstructure, or superhelix. The lamellar and superhelix structures of amylopectin are only a small part of the whole picture, however. On a larger (microscopic) scale, it is known that starch granules are made up of alternating amorphous and semi-crystalline shells, between 100 and 800 nm thick. These structures are termed growth rings. Almost nothing is known about the amorphous parts of the growth rings. The more crystalline regions, however, can be studied by X-ray diffraction. Recently experiments using extremely focused X-ray beams at a synchrotron have demonstrated that within the semi-crystalline regions, the nanoscopic lamellae are parallel to the surface of the starch granule. This provides a way to link the small (microscale, e.g. the starch granules) and the very, very small (nanoscale, e.g. lamellae) – a link that is difficult to obtain in such structural investigations. Another recent study, using atomic force microscopy to look at the starch granule's surface, showed the presence of blocklets within the growth rings. These blocklets are more or less spherical and have a size of 20–100 nm. Nothing more is known about these blocklets, for the moment. It may be hypothesized that the architecture of blocklets follows phyllotactic patterns as a result of the emergence of self-organizing processes in dynamic systems. Taking all the studies together, one can be fairly sure about nanoscale structure (double helices forming lamellae) and the growth rings (alternating amorphous and semicrystal line shells); however, the evidence for the intermediate structures (the superhelices and the blocklets) is less solid.

Furthermore, it is still unclear how the superhelices, blocklets and growth rings relate to each other. The different structural levels (glucose units, helices, lamellae, superhelices, blocklets and growth rings), from the molecular (10^{-9} m) to the microscopic (10^{-5} m) level are summarized below.



As early as 1858, the Swiss botanist Carl von Nägeli had a brilliant intuition, stating that “The starch grain...opens the door to the establishment of a new discipline... the molecular mechanics of organised bodies.” He would no doubt be astonished that, more than 150 years later, we are still struggling to understand the complex architecture of starch granules. The presentation will review and distinguish between those structural features that have received widespread acceptance and those that are still under debate, with the ambition of being educational and to provide stimulation for further fundamental investigation into the starch granule as a multi-scale macromolecular assembly.

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Serge Perez was born in Perigueux, France, and graduated, in crystallography, from the University of Bordeaux, France. He then spent one year at the Institute of Molecular Biology at the University of Oregon, Eugene, USA and subsequently three years at the Department of Chemistry at the University of Montreal, Canada. He returned to France upon accepting a permanent position as a Junior Scientist of the Centre National de la Recherche Scientifique (CNRS) at Centre de Recherches sur les Macromolécules Végétales (CERMAV), Grenoble, and he spent a sabbatical year working for Eastman Kodak in Rochester, USA. Later on, he moved on to Nantes, France, at the Institut de la Recherche Agronomique, where he was awarded a position as Senior Research Scientist to start a research group in Molecular Engineering. In January 1996 he moved back to Grenoble to become Chairman of the CERMAV, and hold this position for 11 years. He left this position to the European Synchrotron Radiation Facility to take up the position of Scientific Director in charge of the Life Sciences, Chemistry and X-ray Imaging programs. After completing his term, he returned to the CERMAV in 2012. Since January 2014 he is a staff member of the Department of Molecular Pharmacology, a joint research unit between CNRS and University Joseph Fourier in Grenoble.

His research interests span across the whole area of structural and conformational analysis of oligosaccharides, polysaccharides, glycoconjugates and protein-carbohydrate interactions in solution and in the solid state. This includes interests in computational chemistry and molecular modeling, crystallography, NMR spectroscopy, along with the structure-function and structure-properties relationship. He is the author of more than 250 research articles, review articles and book chapters in this area, which gave rise to about 9000 citations. Beside his broad range interest in the field of

structural glycoscience, Serge Perez is involved international and international committees related to the evaluation of scientific research and to the structuring of multilateral collaborative schemes. He is also involved in management duties at the doctoral levels and in the creation of glyco-biotechnology companies. He is also the founder of the internet site : glycopedia.eu, a recent initiative which addresses aiming at promoting the field of glycoscience throughout the publication of educational e-chapters and the publication of e-news.

2.3. Katja Loos, AG Groningen (The Netherlands)

Physical properties and structure of enzymatically synthesized amylopectin analogs

The most popular and most developed method for determination of the size distributions of natural polysaccharides - such as starch - is size-exclusion chromatography (SEC). Well-defined synthetic (hyper)-branched polymers such as amylose and amylopectin analogs are more advantageous for molecular size distribution characterization and the establishment of new techniques than natural polymers due to their better solubility in water and tunable degree of polymerization and degree of branching.

In this study we concentrated on synthetic polysaccharides in order to obtain and compare all available data for different distributions and size dependence of molecular weights. Amylopectin analogs were synthesized via an *in vitro* enzyme-catalyzed reaction using the enzymes phosphorylase *b* from rabbit muscle and *Deinococcus geothermalis* glycogen

branching enzyme. The synthesized polymers had a tunable degree of branching (2% ÷ 13% - determined via ^1H NMR) and tunable degree of polymerization (30 ÷ 350 - determined via UV spectroscopy). The systems used for separation and characterization of the synthesized branched polysaccharides were SEC-DMSO/LiBr with a multi detection set-up (refractive index detector, viscosity detector and multi angle light scattering detector); and SEC-water/0.02% NaN_3 ; and SEC-50mM NaNO_3 /0.02% NaN_3 with multi detection. Additionally the side chain length distributions of enzymatically debranched polysaccharides were investigated by MALDI ToF MS analysis.

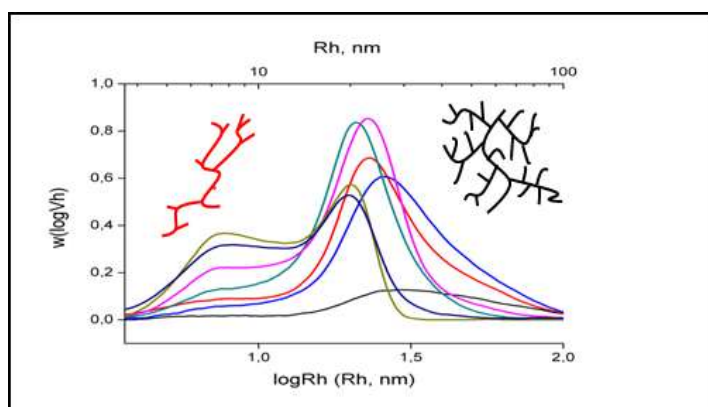


Figure 1: SEC weight distributions of the enzymatically synthesized branched polysaccharides

With this combination of characterization techniques we were able to not only characterize the amylopectin analogs but also to solve parts of the molecular mechanism of their enzymatic polymerization. Additionally our samples show an excellent potential to be characterization standards for the field of starch characterization.

Acknowledgement:

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Katja Loos is Professor at the Polymer Chemistry Department (University of Groningen), The Netherlands. Her main interests are different enzymatic polymerizations and polymer modifications, biocatalytic synthesis of monomers and polymers, the interaction of proteins with specialized surfaces, living polymerizations and block copolymer self-assemblies. She specialized in Organic and Polymer Chemistry at the Johannes Gutenberg Universität (Mainz, Germany) & the University of Massachusetts (Amherst, USA) and moved into the field of Enzymatic Polymerizations during her doctoral research at the University of Bayreuth (Germany) & the Universidade Federal do Rio Grande do Sul (PortoAlegre, Brasil). After a postdoc (Humboldt Fellow) at the Polytechnic University (Brooklyn, NY, USA) she started a research group at the Zernike Institute for Advanced Materials (University of Groningen). She is an VIDI nad VICI laureate of the Netherlands Organisation for Scientific Research and a Fellow of the Dutch Polymer Institute.

2.4. **Chi-Wah Yeung** und **Hubert Rein** Bonn (Germany)

Assay of surface energy of starch

Starches for pharmaceutical applications like e.g. tableting (disintegrants) or hot-melt extrusion are well established. A certain amount of native starches (corn starch, potato starch, pea starch, wheat starch, rice starch) are registered in the European Pharmacopoeia (Ph. Eur.). In this presentation, the focus should be set on the surface energy determination from different types of corn starches. Surface tension assists to solve questions about the wetting-effect between liquids and diverse materials. Here fore, the contact angle Θ is important. A value about 0° means a complete spreading, whereas 90° stands for a worse wetting.

For the performance of surface measurement, the capillarity method (Washburn according to Ph. Eur.) was used. Starch powders were filled in a glass tube and brought in contact with wetting agents. The liquid n-Hexane has a dispersive fraction of 18,4 mN/m, whereas water possesses a polar fraction of 51 mN/m and a dispersive part of 21.8 mN/m. Addicted to the powder content, varying wetting behaviours can be observed.

The solid active pharmaceutical ingredient acetylsalicylic acid (ASA) in contact with water reveals a $\Theta \geq 88^\circ$. This explains its preferred solubility in an organic solvent than in water, while ASA belongs to the biopharmaceutical classification system I (high solubility & high permeability).

Native corn starch, waxy corn starch, high amylose corn starch, potato starch and pea starch were investigated. Depending on different compositions inside starches e.g. proteins and fats, contact angles Θ between 60° and 80° were measured.

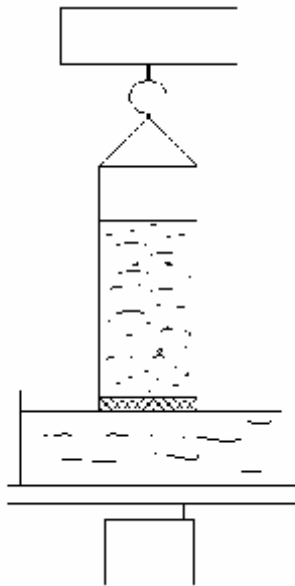


Figure 1 Washburn method

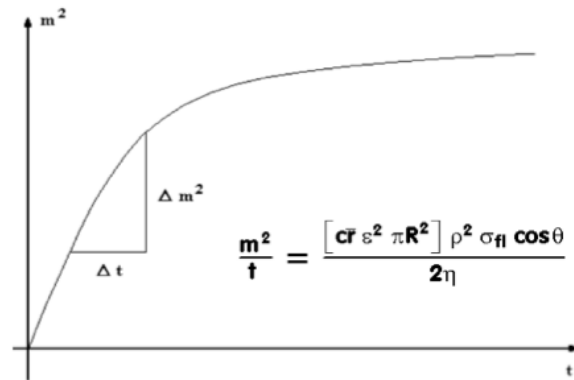


Figure 2 Increase of mass [m²] regarding to time [t]



Chi-Wah Yeung studied pharmacy at the University of Bonn, Germany. In 2011, he began his PhD study in the working group of PD Dr. Hubert Rein. He is working on hot-melt extrusion of different polymers like starches. Furthermore, he investigates the surface tension of APIs and excipients.

2.5. **Marcela Slukova, Josef Prihoda and Iva Honcu**, Prague and **Miroslav Kubin**, Usti nad Labem (Czech Republic)

The effect of bakery improvers on staling of wheat bakery products

Staling is a complex process that starts immediately after bread baking when products are cooled. It can be described as common result of physical, chemical and sensorial changes affecting the consumer's acceptability of baked product. Despite a phenomenon of bread staling has been described for more than one century, up today it was not explained fully in details. A retrogradation or recrystallization of starch granules is supposed as a main reason of staling.

The partly crystalline microstructure of starch granules is changed to disorder during baking process, mainly due to the migration of water molecules inside the structure. At the temperatures more than 60 °C gluten gel is denatured and water is transferred to starch granules and serves to its gelatinization. During cooling after baking, water starts to migrate back to its original partly crystal lattice.

Sensorial changes of baked products are caused by several effects. Firstly by the loose of moisture in crumb, secondly by the retrogradation of starch granules. At the moment of end of baking the moisture profile is not balanced inside the crumb. Moisture in the middle is highest and structure is not solid enough. Water migrates to the crust and in part is lost by evaporation during cooling. Crumb consequently hardens and its toughness or chewiness is changed due to retrogradation of starch too.

Staling speed of bakery products depends considerably on the storage conditions, predominantly on the temperature and moisture. Retrogradation of amylose starts very early after cooling of product and is faster than that of amylopectin. The highest speed of retrogradation is at the temperatures about 4 °C, at temperatures over 20 °C is considerably slower.

The staling of bakery products could be retarded by addition of some bakery improvers such as enzymes (amylases, lipases, proteases, pentosanases), emulsifiers, hydrocolloids (derivatives of cellulose, fibre etc.).

Aim

The aim of the work was to observe the staling process of small wheat rolls and sweet wheat bakery products. The effect of different bakery improving mixtures (mixture of enzymes and emulsifiers) was evaluated on retardation of staling process in crumb and prolongation of the shelf-life of the bakery products has been assessed. Staling of bakery products was watched for 5 days by measuring the crumb firmness (penetrometry measurements), changes in crystallization of amylopectin (x-ray diffraction), and changes in polymers microstructure by scan electron microscopy (SEM) and by FT-IR spectrometry. The new modified method of measurement of crumb viscosity aqueous suspension of crumb at 30 °C was tested as a measure of the range of starch gelatinization in the crumb. The sensorial properties were determined in fresh and staled bakery products too.

Experimental procedure and methods

The dough formula used in this study comprised standard white wheat flour, yeast, plant oil, salt, sugar, ascorbic acid, improver (enzymes, emulsifiers, malt, xanthan), and water (to reach the standard dough consistency). Dough was prepared with different type of improvers and baked products were evaluated during their staling.

All the ingredients were mixed for 10 min (Spiral Mixer). Dough was proofed for 15 min (30 °C, 80% humidity) and shaped. Dough pieces were proofed at 30 °C and 80% humidity and baked at 230 °C. After cooling the small wheat rolls and sweet wheat bakery products were analysed. Sensorial evaluation of baked products was done after 1, 2, 3, 4, 6, 8, 12, 24, 48 and 72 h and at the same time the crumb of baked products was evaluated by promylograph (Promylograph T2-E, Max Egger, Germany) and penetrometer (PNR-12, Petrotest Instruments, Germany). Specific volume of baked products was determined also too. The changes of starch structure in staling crumb were observed by scanning electron microscopy (SEM) (scanning electron microscope TESCAN VEGA3 LMU, tungsten cathode), x-ray diffraction (XRD diffractometer PANalytical X'Pert PRO, PANalytical, Netherlands) and FT-IR spectroscopy (Perkin-Elmer, USA) during 5 days. The water activity and dry matter of crumb were measured during staling.

There is a partly gelatinized starch in fresh baked products and after baking the starch structure returns in organized structure. Consequently, the crumb viscosity changes during staling. The new modified method of measurement of crumb viscosity aqueous suspension of crumb at 30 °C was tested as a measure of the range of starch gelatinization in the crumb. Changes of maximum viscosity peak has been proposed as indicator of crumb staling. It is supposed that maximum viscosity peak decreases due to the hardening of partly gelatinized starch granules during staling.

Results and discussion

The rate of changes in crumb firmness, amylopectin crystallinity and rigidity of polymers were biggest for the control wheat bakery products without improvers during storage.

Sensorial evaluation of baked products was carried out according a hundred-point system (scoring system). Appearance, volume and shape, crust and crumb colour and flavour and taste were evaluated after 1, 2, 3, 4, 6, 8, 12, 24, 48 and 72 h. The lower

score meant the worse quality and the shorter shelf-life of bakery products. The decrease of sensory acceptability of bakery products was found out during staling.

The relationship between amylographic maximum and staling process was proved. The lower decrease of amylographic maximum indicated the slower staling of bakery products. The correlation coefficients among results of sensorial evaluation and promylographic (viscoamylographic) parameters were high and significant.

The crumb firmness (measured on penetrometer) increased on time during staling. The higher of penetration depth to crumb indicated the slower staling process. The significant differences among the used single improvers and staling process were not found. The relationship between crumb firmness (measured on penetrometer) and maximum viscosity peak (measured by promylograf) was found.

The relationship between crumb firmness and relative crystallinity of starch were observed by x-ray diffraction during staling. The increase of starch crystalline phase in crumb of staled bakery products was observed. The higher peak intensity and the higher peak area (characterizing the crystalline phase of starch) were evident during staling process. The differences between used single improvers were showed recognizable. The crystallinity of starch crystalline phase was increasing in time, the starch crystalline phase was higher and/or the internal organization in starch crystalline phase was more regular. Total mass crystallinity grade and relative crystallinity increased only in the first 24 h.

The conformational changes in starch and water distribution in crumb were compared by FT-IR spectrometry in fresh and staled bakery products. Fourier transform infrared spectra (single ATR technique) demonstrated the retrogradation of starch by changes in peak line shapes and intensities in the characteristic area between 995 cm^{-1} and 1050 cm^{-1} . The conformational changes in starch molecules occur during staling. The absorption band at wavenumber 1047 cm^{-1} (corresponding to crystalline phase of starch) was increased and the absorption band at 1022 cm^{-1} (corresponding to amorphous phase of starch) decreased during staling. The absorption band at wavenumber 998 cm^{-1} was assigned to structural changes in crumb which were caused by moisture movement (redistribution of water in crumb of staled bakery products).

The changes in shape of starch granules and changes in structure of crumb of staled bakery products were showed by scan electron microscopy. The gradual deformation of starch granules and break of linkage between starch and gluten was observed during staling. The significant differences among the used single improvers and staling process were not found.

Conclusions

The measurements on promylograph, penetrometer, x-ray diffractometer, FT-IR spectrometer and scan electron microscope were successfully used for the evaluation of the staling process in crumb of wheat bakery products. This way, the effect of different bakery improvers on staling of the bakery products was tested and proved. The results of instrumental analyses were confirmed by sensorial evaluation. The significant relations between promylographic and sensorial evaluation were found.

New modified method of promylographic viscosity measurement of crumb aqueous suspension of bakery products was successfully verified. Consequently, promylographic analysis and penetrometer measurements can be considered good techniques to test staling and shelf-life of bakery products. The devices could be recommended for practice in cereal technology.

The study about staling of wheat bakery products was carried out in co-operation with ICT Prague and industrial Czech bakery MILLBA-CZECH.



Marcela Slukova, PhD., 2000-2003 postgraduate study, Institute of Chemical Technology (ICT) Prague, Faculty of Food and Biochemical Technology, Department of Carbohydrates and Cereals, Dissertation work (2003): Polysaccharides in foods and their identification
2003-recent Assistant Professor, fields of specialization: cereal chemistry and technology, quality of cereal raw materials and products, food nutrition with focus on saccharides and dietary fibre

3. Modification

3.1. **Mohammad Naushad Emmambux**, Pretoria (South Africa)

Starch modification with stearic acid for 'clean' label starches

Introduction:

Starch is widely used in the food industry for thickening, stabilizing and even as a fat replacer. These starches are generally modified with chemicals to produce substituted and cross-linked starches for better functionality and stability. The production of these starches require the use of 'non-food friendly' chemicals with legislative limitation and the use of solvents that require disposal. They are also not regarded as 'clean' label. This presentation discusses starch modification using lipids as food biomolecules.

Methods:

Normal maize starch (10 % solid) was modified with stearic acid (a lipid molecule) at 1.5 % (w/w) for 30 and 120 minutes at 90 °C in a rapid visco-analyser to determine the pasting properties. The paste was then undigested and digested with thermostable alpha amylase and then analyse with XRD (X-Ray diffraction) and DSC (differential scanning calorimetry). The pastes were also used to replace oil by 50 and 80% in a low calorie mayonnaise type emulsion (LCMTE). The flow properties and the light microscopy with confocal laser scanning microscopy were done to evaluate the LCMTE.

Results and discussion

When starch is modified with stearic acid, a biphasic starch paste (two pasting peak viscosity) is obtained. The second pasting peak viscosity is characterised by high viscosity and non-gelling properties. These properties seem to be similar to (i) substituted starches which are non-gelling and (ii) cross-linked starches with high viscosity. The non-gelling and high viscosity of starch modified with stearic acid is due to the production of amylose-lipid complexes (ALC) as shown by X-ray diffraction and differential scanning calorimetry. Distinct V-amylose diffraction patterns for the starch pasted for a prolonged time (120 min) with added stearic acid while less-distinct V-amylose patterns with non-complexed stearic acid peaks were observed with a short pasting time. Differential scanning calorimetry (DSC) before and after paste hydrolysis showed that amorphous Type I amylose-lipid complexes are present in the paste formed at the short pasting times, while semi-crystalline Type II complexes are present in the second paste viscosity. The amylose lipid complexes are at nanometer scale and this can also allow for more interaction in the system for higher viscosity.

When the starches was used as fat replacer, LCMTE with modified maize starches had lower yield stress and viscosity, and larger oil droplets compared to LCMTE with unmodified and maize starches. Increasing oil replacement level (50% to 80%) increased the viscosity. At 50% oil replacement, unmodified and modified maize starch with stearic acid could produce LCMTE. When the oil content was further decreased to 80% only the LCMTE with modified starches were similar to the full fat.

Conclusions:

Starch modified with lipids may be considered as food friendly chemicals and regarded as 'clean' label starch for food application for example production of LCMTE.



Dr Mohammad Naushad Emmambux is currently a senior lecturer at the Department of Food Science, University of Pretoria. He lectures in food chemistry, and cereal science and technology and research on the chemistry, functionality, rheology and nanotechnology of starch from indigenous African cereal. He has several publications in peer reviewed scientific journals, and currently supervising/co-supervising 8 MSc and 7 PhD students.

3.2. **Oluwatoyin A. Odeku**, Ibadan (Nigeria) and **Katharina M. Picker-Freyer**, Halle/Saale (Germany)

Natural and modified yam starches as directly compressible excipients in tablet formulation

Yams are staple root crops cultivated in many parts of Africa and Southeast Asia, belonging to the genus *Dioscorea* which includes more than 600 species. Yam tubers are rich in starch (70 - 80 % dry basis) and are usually consumed as food in the forms of flour, fufu, and slices resulting from any of the processes of boiling, drying, fermentation, frying, milling, pounding, roasting, and steaming. However, yams are highly perishable due to their high water content and an estimated annual loss of 10-60 % of total crop has been reported. Conversion of yams into starches will reduce the loss and add value to the crop. In the present study, starches from one of the under-utilized specie of yam, *Dioscorea dumetorum* (generally known as bitter yam) was extracted and modified using chemical (acid hydrolysis, hydroxypropylation and crosslinking) and physical (gelatinization) methods and evaluated as directly compressible excipient in pharmaceutical tablets. The results showed that the material properties and compressibility of the starches varied considerably depending on the type of modification the starch was subjected to. Chemically modified starches yielded tablets with acceptable crushing strength and fast disintegration time while the pregelatinized starch yielded non-disintegrating tablets that could be suitable for controlled release formulations. The modified forms of bitter yam starch could be more useful than the natural form as directly compressible excipient depending on the intended use of the tablets.



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3.3. **Christina Gabriel, Henning Winkler, Rainer Rihm and Waltraud Vorweg**, Potsdam (Germany)

Optimized starch esters for materials

With its worldwide availability and its low market-price native starch provides the potential for the use as a biobased material. Because of its combination of a high glass transition temperature and an early degradation, for film preparation or extrusion processing the use of plasticizers is required. However, the chemical modification of starch, e. g. esterification, offers the opportunity to produce thermoplastic processible starch derivatives without the use of plasticizers.

For this purpose, starch (Gelose 80, starch with 80 % Amylose) was modified by carboxylic acid vinyl ester transesterification after dissolution in DMSO using a basic catalyst. The chain length of the ester groups was diversified from C2 to C8 and C12. The DS-values were determined by the methods elementary analysis, ¹H-NMR spectroscopy and saponification with subsequent acid-base titration. Depending on the chain length and the DS-values the prepared starch esters possessed solubility in THF or CHCl₃ and could be processed to films by solution casting. The mechanical properties of these films were investigated via tensile tests with the Zwick 1445 universal testing machine according to DIN EN ISO 527. Data of tensile strengths in the range of 8.4 to 68.5 MPa as well as tensile strain in the range of 0.6 to 36.3 % were achieved and influenced by the sort and the DS of the ester groups. The thermal properties of the starch esters were studied with TGA and DSC. For the thermal degradation temperatures > 300 °C were obtained. Hydrophobicity of the films was evaluated by contact angle measurements. All selected films showed a contact angle larger than 90°.

The investigations showed that the starch hexanoates with the DS-values of 1.50, 1.60 and 1.70, the octanoate with the DS of 1.07 and the laurate with the DS-value of 1.03 exhibit the potential for a thermoplastic, plasticizer-free processability (extrusion). Additionally they all possessed comparable tensile strength to LDPE (25 MPa).



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3.4. **Andreas Blennow**, Frederiksberg C (Denmark)

Clean modification of starch using a semi-solid-state branching enzyme-assisted protocol

Chemical cross-linking of starch is an important modification used in the industry for granule stabilization. We are demonstrating that treatment with branching enzyme (BE, α -D-1,4 \rightarrow α -D-1,6 glycosyltransferase), if used at extreme starch dry matter content (30–40%, w/v), can stabilize the granular structure of starch and such treatment thereby provide a potential clean alternative for chemical modification. Bright field/polarized light and scanning electron microscopy confirmed maintenance of granular structure. The product compared to the control had significantly increased degree of branching, size exclusion chromatography demonstrated the presence of uniform molecules with smaller size and polysaccharide product was more soluble at than the corresponding heat-treated control. The granule stabilizing effects were decreased by hydration of the starch granules, which was increased by the presence of starch-phosphate esters, typically present in tuberous starches like potato starch, and suppressed by extreme substrate concentration. The data support that the granule stabilization is due to the intermolecular transglycosylation occurring in the initial stages of the reaction prior to amylopectin–amylose phase separation. The enzyme activity needed to obtain granule stabilization was therefore dependent on the hydration capability of the starch used. A hypothetical model is presented to account for the observed phenomenon.

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Andreas Blennow received his PhD in Biochemistry in 1992 at Lund University, Sweden, is now heading the Starch Group at Copenhagen University. His main research interests are within starch bioengineering including resistant starch produced directly in crops with transgene and mutant technology and starch structure-function modeling related to food starches and biomaterials.

3.5. **Hanna Staroszczyk**, Gdansk (Poland)

Rheology of potato starch chemically modified with microwave-assisted reactions

Chemical modification of starch with at least dibasic acids, their anhydrides and salts, provides ester-type derivatives of starch of anionic properties. Such properties are crucial for intermolecular interactions with other, oppositely charged macromolecules, for instance, with proteins. In such manner binary systems are formed which combine properties of both partners. Enjoying a wide potential application, biodegradable polysaccharide-protein materials can be derived from them, and modified starch can contribute to the improvement of their functional properties.

It was found that microwave irradiation offers a facile synthesis of starch esters, including inorganic starch esters such as sulphates, borates, selenates, silicates and zincates. The rheological properties of these starch derivatives are important for their handling, processing and utilization. In this presentation an influence of esterifying agent on potato starch rheological behavior is presented.

The flow behavior index and the consistency index were determined by applying the power law, and the plastic viscosity and the yield stress were evaluated from the Cassone model. The results obtained showed that although the tested pastes of potato starch differ in terms of shear rates, most of them are non-Newtonian and shear thinning fluids with the yield stress. The variation of parameters calculated from both models, and also chromatogram profiles and plots of differential molar mass distribution versus molar mass obtained by using high performance size exclusion chromatography, indicated that during the microwave-assisted esterification of starch with the investigated compounds the processes of starch substitution, crosslinking and degradation take place.

In contrast to short microwave irradiation, the prolonged radiation of potato starch leads to

an increase in the value of the flow behavior index, and a significant reduction in the values of all other rheological parameters. Thus, with increasing irradiation time, starch pastes become more resistant to thinning by shear forces, less viscous and more susceptible to deformation – their yield stress completely vanishes. Such changes indicate that starch degrades. This is confirmed by decreasing values of the molecular weights of the polymer with increasing time of microwave irradiation.

Significantly reduced, relative to native starch, molecular weight values of starch sulphated with $\text{SO}_3 \times$ pyridine complex and borated with boric acid, show that the acid-catalyzed decomposition of starch is the predominant process occurring during the formation of these derivatives. This contributes to a significant reduction of the starch paste viscosity and leads to a decrease in the examined rheological parameters: the consistency index, the yield stress and the plastic viscosity. During starch silication, as well as boration with borax, selenation and zincation, the variation of the rheological parameters and the evaluated values of the molecular weights show that the decomposition of polysaccharide is accompanied by crosslinking. At lower concentrations of esterifying reagents crosslinking prevails, while at higher

concentrations the process of decomposition dominates. The decomposition is caused by NaOH that is formed during the reaction.

Both the microwave irradiation itself, and the microwave-assisted esterification of potato starch with the compounds used, does not affect the relationship between the apparent viscosity and temperature. However, the intensity of the viscosity changes is largest in the case of native starch pastes. The highest are also the values of the activation energy of the flow of those pastes, determined from the Arrhenius equation. These results confirm a greater susceptibility of native starch pastes to the viscosity change with temperature in comparison to the modified starch.

The chromatogram profiles implied that amylose and amylopectin fractions in starch molecules are retained after its microwave irradiation. However, the shape of curves showing the relationship between the differential molar mass distribution and the molar mass indicates that the number of starch molecules coming from the amylopectin fraction considerably decreases as early as after several minutes of the irradiation, and an extension of this period leads to fragmentation of the polysaccharide chains of the polymer from that fraction.

In the case of starch modified with the reagents examined, differences in the chromatogram profiles obtained show that while the lower concentration of esterifying reagent retains amylose and amylopectin fractions in the starch molecules, the higher concentration of these reagents result in simultaneous processes of substitution, cross-linking and degradation of starch. The analysis of the plots of the differential molar mass distribution versus molar mass for starch silicated with sodium metasilicate and the zincated starch indicates that the number of starch molecules of the amylopectin fraction is reduced on esterification. Thus, it can be assumed that starch esterification with the reagents examined results in the products in which acidic moieties are more often arranged along the linear chains than along the branched ones.

Hanna Staroszczyk is an associate professor at Gdansk University of Technology, Poland, where she received her D.Sc. in technological sciences for research in starch chemical modification. Her professional career is also associated with Agriculture University in Krakow, where she obtained a Ph.D. in agricultural sciences for research on polysaccharide-protein complexes. Her current research interests include starch modifications and biodegradable plastics.

3.6. **Andreas Blennow**, Frederiksberg C (Denmark) Engineering an amylose-only cereal starch

Starch is a multipurpose polysaccharide with tremendous importance within food, feed and fuel and is now increasingly developed for advanced renewable materials applications. Direct starch bioengineering of cereals is emerging following progress in our understanding of starch biosynthesis, and genes involved in this process permitting genetic modification of crops in a rational manner to produce novel designer starches with new and improved functionality. We used barley as a model and targeted two important starch features, the phosphate content which has potential industrial applications and amylose content having valuable food, feed and biomaterial applications. To this end, we overexpressed the potato starch phosphorylation enzyme, Glucan Water Dikinase (GWD) and suppressed the 3 existing isoforms of starch branching enzyme (SBE) by RNAi technology, in barley. We reached a 10-fold increase in starch-phosphate content and ~99% amylose content, respectively, in in our transgenic barley lines. For the ~99% amylose line, amylose-only, AO) in vitro enzymatic starch hydrolysis showed 2.2-fold higher resistant starch than the control starch. Our approach can be extended to other cereal systems and we thoroughly tested possible side effects using microscopy, chemical compositional analysis and GC-MS metabolite profiling approach to verify GM “substantial equivalence” criteria for the

new lines. Typically, the AO line showed reduced yield and starch content and higher and altered sugar composition.

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Andreas Blennow received his PhD in Biochemistry in 1992 at Lund University, Sweden, is now heading the Starch Group at Copenhagen University. His main research interests are within starch bioengineering including resistant starch produced directly in crops with transgene and mutant technology and starch structure-function modeling related to food starches and biomaterials.

4. Green Chemistry

4.1. Robin D. Rogers, Tuscaloosa (USA)

Advanced Materials from Renewable Polymers: Why Are We Still Using Synthetics?

With the inevitable depletion of petroleum-based resources, there has been an increasing worldwide interest in finding alternative resources, particularly from renewable resources including lignocellulosic biomass. Clean separation of the three major components of this biomass source is an important and challenging 'Grand Challenge' for the production of reproducible feedstocks for further chemical processing. Chitin, the second most plentiful biopolymer on earth after cellulose, is the most abundant polymer in the marine environment. Crustacean shells are currently the major source of chitin available for industrial processing and annual synthesis of chitin in freshwater and marine ecosystems is about 600 and 1,600 million tons, respectively. The bioactivity, biocompatibility, and low toxicity of chitin make it suitable for commercial use, and contribute to the diversity of over 300 end-use applications, including water treatment, cosmetics and toiletries, food and beverages, agrochemicals, medical/healthcare, and cell culture. However, chitin is produced from the exoskeletons of marine crustacean shell waste by a chemical- and waste-intensive method that involves acid demineralization, alkali deproteinization, and bleaching. The chitin produced still contains trace amount of mineral and protein and quality assurance for final product formulation is of concern.

Even though current 'biorefinery' concepts do emphasize other chemicals besides fuel, it is typically the cellulose and hemicellulose which are utilized in producing paper, fibers, membranes, and other commodity materials and chemicals, while lignin is usually burned for energy. There seems to be relatively little emphasis on using natural biopolymers as polymers rather than feedstock for producing molecular chemical entities.

This presentation will discuss how the components of both lignocellulosic and chitin biomass interact with ionic liquids (ILs) and how these interactions can be used to manipulate solution-properties to process and regenerate biopolymers into a desirable form for specialized applications. The differing solubilities of the biopolymer fractions also allow the exploitation of the IL medium to provide a ready separation mechanism. The unique properties of ILs can be used to provide a platform for biomass to chemicals strategies and yield endless possibilities for forming environmentally-friendly new and enhanced functional materials.



Dr. Robin D. Rogers obtained both his B.S. in Chemistry (1978, Summa Cum Laude) and his Ph.D. in Chemistry (1982) at The University of Alabama and currently serves as Distinguished Research Professor, Robert Ramsay Chair of Chemistry, and Director of the Center for Green Manufacturing at UA. In 2007 he was also Chair of Green Chemistry and Co-Director of QUILL at The Queen's University of Belfast in Northern Ireland (UK) before returning full time to The University of Alabama in 2009. From 2009-2013, he was Honorary Professor at the Chinese Academy of Sciences Institute for Process Engineering in Beijing, China.

Rogers holds 16 issued patents and has published over 725 papers on a diverse array of topics. His research interests cover the use of ionic liquids and Green Chemistry for sustainable technology through innovation and include Materials (advanced polymeric and composite materials from biorenewables), Separations (novel strategies for separation and purification of value added products from biomass), Energy (new lubricant technologies and selective separations), and Medicine (elimination of waste while delivering improved pharmaceutical performance).

He has been cited over 29,000 times and has a Hirsch index of 77. In 2006, Rogers was named a Fellow of the Royal Society of Chemistry and in 2009 was selected to the inaugural class of American Chemical Society Fellows. He was elected a Fellow of the American Association for the Advancement of Science in 2012. In 2010, he was named a Chinese Academy of Sciences Visiting Senior Scientist for the Institute for Process Engineering, Beijing, China. He was awarded the American Chemical Society Separations Science & Technology award in 2011 and in 2012 he was named an ACS Division of Industrial & Engineering Chemistry Fellow.

Rogers is the Founding Editor-in-Chief of the American Chemical Society journal Crystal Growth & Design. He is also an editorial board member of Separation Science & Technology, Solvent Extraction and Ion Exchange, and Chemistry Letters, as well as a member of the international advisory boards for Green Chemistry, Chemical Communications, and ChemSusChem.

He has had an influential role in the expansion of interest and research in ionic liquid systems, his initial paper on ionic liquid/aqueous partitioning (Chem. Comm. 1998, 1765) effectively kick-started interest in applying ionic liquids to clean separations. In 2005 he was awarded the US Presidential Green Chemistry Challenge Award (Academic Division) for work related to the use of ionic liquids in sustainable technology. This technology was licensed later that year to BASF. In 2012, he was named recipient of the Paul Walden Award given by the DFG-SPP 1191 Priority Program on Ionic Liquids.

Rogers has co-organized a variety of meetings and symposia on Industrial Applications of Ionic Liquids and he has started a company (525 Solutions) to enhance the commercial viability of new technologies. The breadth of educational, research, editorial, and service endeavors gives Rogers a broad perspective on science and engineering research, development, and technology transfer

- 4.2. **Tatiana Budtova, Melinda Desse and Dorine Fraiseau**, Sophia Antipolis (France) and **John Mitchell and Bettina Wolf**, Sutton Bonington (UK)
A new approach towards starch granules: flavour perception and controlled release applications

Starch is commonly used in the food industry as a thickening and structuring agent. The way starch systems act when submitted to shear will have a great impact on how food is perceived in the mouth.

In this work we studied the deformation of a single swollen starch granule and of a droplet of suspension made of swollen granules using counter-rotating rheo-optical system. The goal was a) to correlate starch flow properties with the behaviour of one

granule and b) understand the difference between the deformation and break-up of starch suspension droplet and a hydrocolloid solution.

A single swollen-in-water starch granule (modified waxy maize and potato) of different swelling degrees was placed in silicon oil and sheared. It was shown that the granules strongly deform under flow and may eject solvent, which leads to a loss of volume (Figure 1) /1/. This explains a particular rheological response of concentrated starch suspensions. Starch granule can also be used as a delivery matrix for controlled release applications.

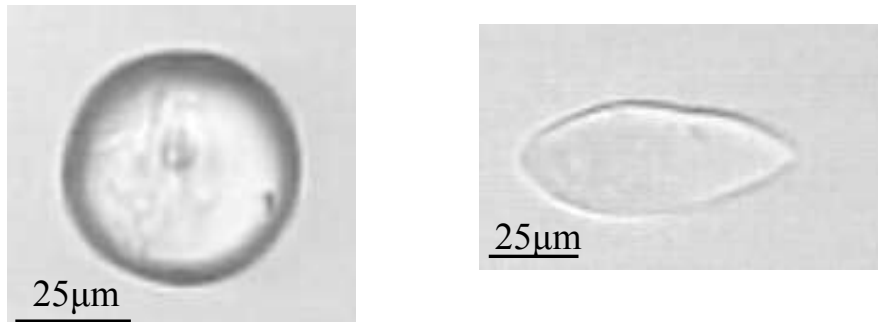


Figure 1.

Shear induced deformation and volume loss of swollen in water modified waxy maize starch granule.

Shear induced deformation and rupture of two types of droplets, hydroxypropyl methylcellulose (HPMC) aqueous solution and modified waxy maize suspension, were studied and compared. A droplet of HPMC solution or a droplet of starch suspension was placed into silicon oil and deformation and break-up was monitored as a function of applied shear stress and strain. It was found that starch suspension droplets broke up at lower deformation stress and strain than HPMC solution droplets (see Figure 2) despite viscosity ratio and capillary number suggesting the opposite /2, 3/. It is hypothesised that the ease with which droplets thickened by starch break up is responsible for their rapid mixing with saliva.

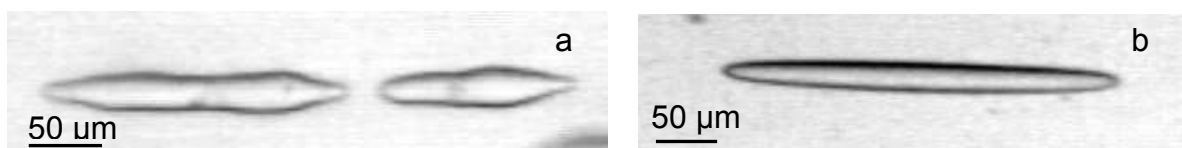


Figure 2.

Demonstration of an « easier » shear induced break-up of starch suspension droplet (a) as compared with no break-up of HPMC solution droplet (b) in the same conditions.

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Tatiana Budtova graduated from physics faculty, Leningrad State University, Russia, and got her PhD degree in polymers (1992) in the Institute of Macromolecular Compounds, Russian Academy of Sciences. In 1999 she got Habilitation in France, in MINES ParisTech. She is working in the area of bio-materials, mainly cellulose and starch (solutions, blends, gels and aerogels) and natural fibre reinforced composites.

5. Application

5.1. Tamara Dapčević Hadnađev and Miroslav Hadnađev, Novi Sad (Serbia) Stabilized starches as bread improvers

Introduction

During the formation and processing of wheat flour dough and its transformation to bread a large number of physical, chemical and biochemical changes on the microstructural level take place (Goesaert et al., 2008). Structure-processing relationship becomes more complex if additives are included into breadmaking, since they change the dough structure and lead to different interaction between dough constituents. The additives are used, first of all for technological reasons. Namely, climate changes are increasingly influencing our food supply chain, since unpredictable growing seasons could not affect only the yield, but also the quality of the wheat crop (Hadnađev et al., 2013). Therefore, additives are necessary to obtain wheat flour lots of uniform quality.

Additives are also used to retard bread stalling, a phenomenon responsible for significant financial loss for both consumers and producers. According to survey carried out in January–March 2010 by the Institute of Food Technology in Novi Sad (Nježić et al., 2010) the amount of leftover bread in Serbia is 25 t of bread per day.

However, recently, there is a trend of using additives in bread production due to nutritive or dietetic reasons. Since, wheat bread is a widely consumed product and staple food in many countries; it is very convenient to be fortified with different fibres, essential fatty acids, minerals, antioxidants, etc. Moreover, enriched bread fits perfectly to changed consumption pattern, where consumers are seeking out healthy food products that contain less fat, sugar and sodium and more functional ingredients.

Recent studies have demonstrated that modified starches can be used as novel additives in breadmaking since they improve bread quality and retard stalling. Modified starches have been originally developed in order to enhance the properties of native starch in specific food and non-food applications, such as to improve its water holding capacity, shear, heat, freeze-thaw and low pH resistance, as well as to reinforce its thickening and binding properties, minimize syneresis, etc. There are several modification techniques which comprise physical, chemical and enzymatic treatment.

Stabilized (substituted) starch such as hydroxypropylated, acetylated and phosphorylated, as well as starch sodium octenyl succinate belong to the group of chemically modified starches in which hydroxyl groups are replaced by new side groups. Since these groups are bigger than –OH groups, they have disruptive structure which inhibits interchain associations which would have occurred in their absence. This characteristic gives these starches unique property such as resistance to retrogradation (Bertolini, 2010; Wrolstad, 2012). Therefore, it is of a great interest to investigate whether stabilized starches would be effective in interrupting the retrogradation of amylose or segments of amylopectin branches during bread stalling.

Literature review - acetylated and hydroxypropylated starches as bread improvers

Investigations performed by group of authors from Japan (Miyazaki et al., 2006) have indicated that bakers can control texture of products, and develop unique bread by using modified starches. Some of the main conclusions extracted from the investigation of the mention group of authors are following:

1. The substitution of wheat flour for 20-30% of hydroxypropylated tapioca starch increases water absorption. However, acetylated starches, generally decrease water absorption of the wheat flour dough at less than 20% of substitution.
2. Bread containing 20% of hydroxypropylated tapioca starch or acetylated tapioca starch and vital gluten is softer than the bread containing wheat flour alone. However, while this softening effect was statistically non-significant for bread containing acetylated starch, it was significant when hydroxypropylated starch was implemented. The reason is the fact that endothermic enthalpy of stale bread baked from substituted flour with hydroxypropylated tapioca starch is smaller than the bread baked from wheat flour alone.
3. However, addition of both acetylated and hydroxypropylated starches into wheat flour led to reduce in specific loaf volume.

Investigations performed by Goesaert et al. (2008) revealed that substitution of wheat starch by hydroxypropylated wheat starch in model bread systems influences initial crumb firmness decrease, but does not have an effect on firmness increase kinetics.

Current investigations concerning starch sodium octenyl succinate as bread improvers

Taking into account the fact that other starch substitutes have exhibited significant bread improving properties and that starch sodium octenyl succinate (OSA starch) has special nutritional values since it can act as functional fibre (Heacock et al., 2004), it was of a great importance to investigate the feasibility of OSA starch as bread improver. The starch sodium octenyl succinate used was obtained from waxy maize starch (C*EmTex 06328, Cargill, France).

Effect of incorporating 10% of OSA starch on dough rheological (creep-recovery measurements) and structural properties, and bread quality parameters (specific loaf volume, crust and crumb colour and crumb texture) was investigated. The following measurements were performed:

1. Structure of the dough substituted with OSA starch was analyzed by Jeol JSM 6460LV scanning electron microscope (Tokyo, Japan). The samples were prepared following the procedure described by Ribotta et al. (2004).
2. Creep and recovery measurements were carried out using a Haake Mars rheometer (Thermo Scientific, Germany) equipped with PP35 S serrated parallel plate measuring geometry (35 mm diameter, 1 mm gap). The measurements were performed at 30 ± 0.1 °C.
3. For breadmaking: the basic bread formula, based on flour weight, consisted of: 300 g of the substituted flours in which 0% or 10% of wheat flour was substituted with the starch sodium octenyl succinates, water, 2.5% fresh yeast and 2% salt.
4. After cooling to ambient temperature (2 h), the loaves were weighed, and their volume was measured by millet displacement method. Bread crust and crumb colour measurements were conducted using a Minolta Chroma Meter CR-400 colorimeter (Konica Minolta Sensing Inc., Japan) (8 mm Ø contact area). Breadcrumb properties were determined by Texture Profile Analysis (TPA) at room temperature by a TA XT2 Texture Analyser (Stable Micro Systems,

England) equipped with a 30-kg load cell and a P/75 – (75 mm diameter) aluminium compression platen (Dapčević Hadnađev et al., 2014). In addition, the changes in crumb hardness during storage (2, 24 and 72 h) were also monitored. The experiments were done on two sets of samples – dough prepared on constant moisture content and dough prepared at constant consistency (water up to 500 BU farinograph consistency).

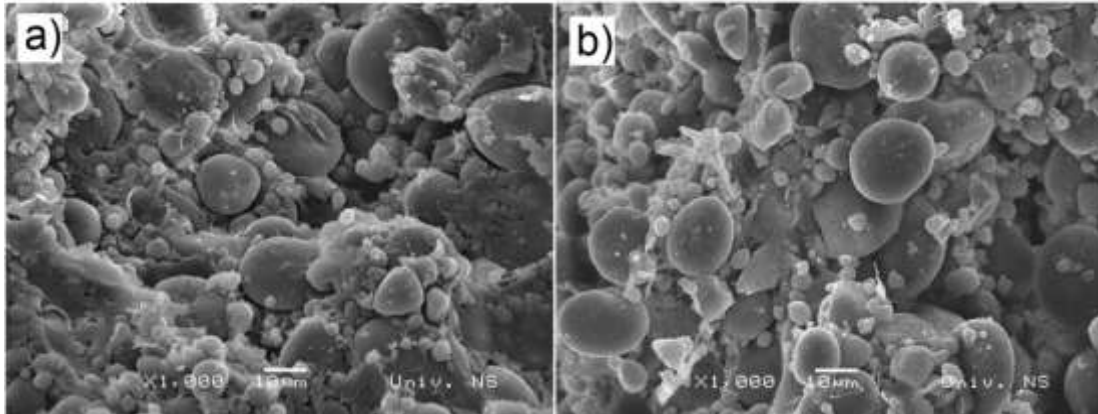


Figure 1. Microstructure of wheat flour dough (a) and wheat flour dough substituted with 10% OSA starch (b)

The results obtained revealed that OSA starch caused a reinforcement of the gluten network, as shown by the decrease in maximum compliance at creep recovery curve. According to SEM image (Figure 1), OSA starch granules were tightly embedded in a reticular protein matrix together with wheat starch granules.

In general (Tables 1 and 2), OSA starch supplemented breads have lighter crust and crumb and this tendency was not influenced by bread preparation method (constant water or consistency). According to Bao et al. (2003), OSA substitution caused a considerable decrease in the extent of degradation of OSA starches by α -amylase, amyloglucosidase, and pullulanase due to the presence of substituents in the starch chains which restrict the activity of the enzymes. This finding can explain lighter bread crusts.

Table 1. Quality parameters of dough and bread prepared at constant consistency

Sample	Control	OSA starch
Dough extensibility - maximum compliance at creep recovery curve, J_{max} ($10^{-5}Pa^{-1}$)	127.5 ^b	74.5 ^a
Crust browning index	88.5 ^b	82.2 ^a
Crumb whiteness index	57.6 ^a	62.4 ^b
Crumb hardness, 2h (g)	14910 ^{b,1}	9879 ^{a,1}
Crumb hardness, 24h (g)	18588 ^{b,2}	11469 ^{a,2}
Crumb hardness, 72h (g)	22270 ^{b,3}	17396 ^{a,3}
Loaf specific volume (cm^3/g)	2.41 ^a	2.50 ^a

Values followed by the same letter in the row or number in the column are not significantly different ($p > 0.05$)

Table 2. Quality parameters of dough and bread prepared at constant water content

Sample	Control	OSA starch
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Dough extensibility - maximum compliance at creep recovery curve, J_{\max} (10^{-5}Pa^{-1})	152.14 ^b	86.38 ^a
Crust browning index	72 ^b	69.6 ^a
Crumb whiteness index	64.0 ^a	65.3 ^b
Crumb hardness, 2h (g)	9390 ^{a,1}	11245 ^{b,1}
Crumb hardness, 24h (g)	14983 ^{a,2}	18901 ^{b,2}
Crumb hardness, 72h (g)	18675 ^{a,3}	22549 ^{b,3}
Loaf specific volume (cm^3/g)	3.60 ^b	3.40 ^a

Values followed by the same letter in the row or number in the column are not significantly different ($p > 0.05$)

However, breadmaking procedure has significant influence on quality parameters such as specific loaf volume and changes in crumb texture as indicator of bread stalling. When breadmaking was performed at constant consistency, OSA starch acted as bread improver. These results could be explained by the fact that OSA supplemented dough expressed improved water absorption, (56.1% in contrast to control flour with WA of 55.4%) and consequently, increased water content in bread crumb, which therefore was less dry and more tender. In the system with restricted water content the remaining ungelatinized starch granules in crumb were considered to be some of the factors that make texture of bread hard.

Further investigations using flours of different quality and OSA starches of different botanical origin are needed in order to obtain complete information concerning OSA starches as bread improvers.

Acknowledgements

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Dr. Tamara Dapčević Hadnađev, Head of Rheology Lab, Institute of Food Technology, University of Novi Sad, Serbia

Research associate in the field of: rheology, texture and structural properties of food; mostly rheology of starch, wheat and gluten-free dough, hydrocolloids and emulsions. Design and characterization of functional food with the special interest in food structure-property relationship.

5.2. Evžen Šárka, Petra Smrčková, Meltem Saglamtas and Jaroslav Kolářek, Praha (Czech Republic)

Influences on digestibility of corn grits during extrusion – process parameters, native or modified starch addition

Starch is the main component of digestible carbohydrates consumed in the human diet and can generally be classified as rapidly digestible (RDS), slowly digestible (SDS) and resistant starch (RS) according to its susceptibility to pancreatic amylase (in vitro). RDS is degraded to glucose in 20 min after enzymatic activity. SDS is changed into glucose while being digested in the small intestine for up to 120 min and has beneficial physiological effect on the reduction of post-prandial glycemic responses. RS escapes digestion by human enzymes within the small intestine and passes into the colon, where it is metabolized into secondary products by colonic microflora and behaves in a way similar to dietary fibre. It reduces the calorific value of the food and is assumed to have an important role as an agent protecting against colorectal carcinoma, the incidence of which is very high in the Czech Republic.

Extrusion cooking may be defined as a continuous process in which raw materials are forced through an orifice and transformed into cooked and formed products. Due to thermal treatment, high pressure and shear forces, starch granules disrupt and merge into dispersion (gelatinisation). The process is connected with molecular fragmentation of starch polymers, which ameliorates starch retrogradation. Many authors report a decrease in RS content (or increased digestibility) after extrusion processing. Further changes during extrusion are protein denaturation and the formation of complexes between the lipids and starch and/or proteins.

The integrity, and thus digestibility, of starch granules depends on such conditions as water content, temperature, cooking time, pressure, and pH. E.g. low initial water content in raw material for snack food predetermines that this process will result in products having a high content of slowly digestible starch. The extent of cooking reactions also depends on the construction of the apparatus employed.

Besides the nutritional values of the extrudates, important parameters are sensorial and mechanical ones, e.g. colour, flavour, shear stress-at-break, water solubility index, rehydration and expansion ratio (ER = diameter of product/diameter of die opening).

The aim of the work was to seek suitable conditions for saving resistant starch and/or for increasing the content of slowly digestible starch (SDS) in the extrudate compared to raw materials such as maize grits, as well as to other mixtures with added wheat starch, pea flour or chemically modified starch. Extrusion of the wetted premix was performed using a laboratory single-screw Kompaktextruder KE 19/25 (Brabender, Germany). The extruder was used at different speeds (120 – 140 rpm) of the screw with either a 2:1 or 3:1 compression ratio; the head had a 3 or 4 mm die. The temperature of the head was set at 131 – 144°C. The input mixtures differed in composition and water addition (5, 10, 20% wt.).

The best organoleptic and nutritional results of extrudates were found using a die with a 3 mm diameter and a screw with a 3:1 compression ratio, the temperature of the head was approximately 140 °C. Transportation rates: screw 140 rpm, dosing 15 rpm.

The best ERs were for 5% water addition and 20%-50% ratio of distarch phosphate (MZBH) in the premix.

During the extrusion process the level of RDS slowly increased and that of RS slowly decreased in all samples. High RS content (3.1% per starch) was found for the 10% water addition and 10% ratio of pea flour in the premix. We can expect similar or even better potential results for high amylose wheat starch. Higher results of RS would be reached using cross-linked starch with a higher degree of substitution as well. A high concentration of resistant starch – 1.9-2.4% per starch – was observed for 20 % ratio of Nutriose (Roquette, France) using 10% water, too. The lowest RS content was registered for pure corn grits using 20% water – 0.08% per starch.

The highest SDS content (72.5% per starch) and 1.1% per starch of RS in extrudates was obtained for the mixture of maize grits, 20% cross-linked starch MZBH and water (10% addition) by the technological parameters described above. The (non-extruded) MZBH has a very high content of resistant starch and therefore it can be suitable for pharmaceutical use without thermal processing.

Acknowledgment

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Evzen Sarka

EDUCATION: MSc. Institute of Chemical Technology Prague; Ph.D graduated in 1983

PRESENT POSITION: Associate Professor at the same university since 2012.

AREAS OF INTEREST: sugar and starch technology, biodegradable plastics, starch digestibility

OTHER: Prof. Sarka is a member of ICUMSA and of ESST (European Society of Sugar Technologists), and of the Scientific Committee of International Conference on Polysaccharides-Glycoscience

5.3. **Maurice Essers, Susann Bellmann, Rob Havenaar and Ted Slaghek,**

AJ Zeist (The Netherlands)

High amylose potato product with low glycemc response and prebiotic effect

Potato consumption represents a significant part of the daily caloric intake of food consumption in large parts of the world. Major components in cooked potato are water (75 wt %), starch (15 wt %), non-starch carbohydrates (e.g. pectin, 2.2 wt %), protein (2 wt %) and fat (0.1 wt %). The current potato varieties contain a high amylopectin content and low amylose content (75-85% and 15-25% of the total starch content, resp.). It can therefore be classified as a vegetable with a high glycemic index (GI) based on the fact that amylopectin is rapidly and almost completely digestible in the human dietary tract. On the contrary, amylose is classified as a resistant starch (type III) and is therefore considered to be an important and strategic component in food as a dietary fiber. The amylose content in current potato varieties is too low to position cooked potato products as a rich source in amylose in comparison to other amylose containing products on the market (e.g. maize products). So, it cannot be positioned as dietary fiber. In order to investigate the potential beneficial health aspect of amylose enriched potato products, TNO and our research partners UMCG, HZPC, and Cosun/Aviko, aimed a proof of concept via in vitro and in vivo studies.

The following approach was taken:

- Isolation of amylose and amylopectin fraction out of potato starch.
- Preparation of potato amylose enriched food products, e.g. potato mash.

In vitro digestibility studies on potato amylose enriched food products by use of Englyst analysis, and the TIMcarbo and TIM-2 systems (TNO's gastro-intestinal model for CHO digestion and a the colon model for fermentation, respectively).

TIMcarbo studies showed that there was a correlation between the amount of amylose in potato based food products and the resistant starch (RS) level; higher levels of amylose resulted in (significant/repeatable) lower levels of digestibility of the potato products. The Englyst analysis showed less consistent results. TIM-2 studies were performed on the fermentation in the colon of undigested carbohydrates from TIMcarbo. Preliminary analyses showed that there was a small increase of the formation of short chain fatty acids (SCFA's) when higher levels of amylose were incorporated in the potato based food matrix. Furthermore, a first human intervention study indicated that amylose enriched, potato based products have a significant lower insulinemic response and a non-significant lower glycemic response.

The results of this program will be used to develop, via selective breeding by HZPC, a high amylose containing potato variety. Further in vitro and in vivo studies should confirm the following positive beneficial health assets:

- Lowering of the caloric value and glycemic and insulinemic response with an impact on prevention of diabetes and obesitas;
- Increasing the content of dietary fibers with a prebiotic effect in the colon.



Born in Maastricht (the Netherlands), I attended the Joan of Arc gymnasium and studied chemistry at the RWTH Aachen. From 1996-2008- industrial career in Paper, sugar and starch industry:

- *More specific:*
- *2006-2009 scientist at SAPPI*
- *2009-2002; R&D industrial starch Cedar Rapids (Cargill)*
- *2002-2003: R&D Krefeld (Cargill-Cerestar)*
- *2003-2008: R&D Tate & Lyle (Syral)*
- *2008- : TNO*

The Focus in my research (present job) is:

- *Development clean green and healthy carbohydrates*
- *Development industrial starches*

5.4. **Peter Köhler**, Freising (Germany)

Wheat Intolerances – Reasons, Consequences and Alternatives

After consumption of wheat-containing products problems occur in a small part of the population. Beside wheat allergy (prevalence about 0.5%) and celiac disease (prevalence about 1%) Non-Celiac Gluten Sensitivity (NCGS) has been confirmed as a true disease condition.

The classical wheat allergy is an immune reaction of the human body towards wheat proteins characterized by the presence of immunoglobulins of the class E (IgE), which can be used as diagnostic markers. Wheat allergy is associated with problems of the skin (urticaria), the respiratory system (baker's asthma) and the digestive tract. Depending on the type of allergic reaction, different wheat protein types may trigger the symptoms (gliadins, glutenins, amylase inhibitors, wheat germ agglutinin, lipid transfer protein, and others).

Celiac disease (CD) is an inflammatory disease of the small intestine triggered by the storage proteins of wheat, rye, barley, and possibly oats in genetically predisposed individuals. This group of proteins (wheat gliadins and glutenins, rye secalins, barley hordeins, oat avenins) is collectively called gluten in the field of CD. Diagnostic markers of CD are IgA and IgG against tissue transglutaminase and deamidated gliadin peptides

as well as endomysium antibodies. A gluten-free diet is currently considered as the only effective therapy of CD and wheat allergy.

NCGS is characterized by a reaction of the human body towards gluten or wheat (not yet clear) independent of allergy or CD. Currently, no diagnostic markers have been identified and, therefore, NCGS can only be diagnosed by ruling out wheat allergy or CD. Beside its impact on human health, NCGS is also of considerable economic importance as the prevalence is estimated to about 6% of the population. This means that there are a high number of patients that need a special diet, which should be low in gluten but not necessarily gluten-free. For a long time NCGS was not taken seriously because people claimed being intolerant against wheat but “ancient” grains such as spelt were tolerated without showing distinct differences in their protein pattern to wheat. Recently, a paper was published that identified amylase-trypsin inhibitors (ATI) as possible triggers for NCGS. ATI are compounds that protect the plant against pests but they have also been described to trigger baker’s asthma, a type of wheat allergy.

For the food industry this situation is a challenge and an opportunity at the same time. Producing high quality gluten-free foods from celiac-safe raw materials as well as from gluten-containing materials rendered gluten-free is an important aim and will lead to improved choices for CD patients. Enzymes, namely prolyl endopeptidases (PEP), play a major role either for deglutenizing gluten-containing foods or as a possible alternative therapy of CD (“PEP pill”). Microbial transglutaminase has successfully been used to produce gluten free beer based on barley malt. Breeding approaches aim at producing so-called synthetic wheat with a low occurrence of CD-active epitopes or at generating ultra-low gluten (ULG) barley, in which the hordein concentration is below the threshold for gluten-free foods. For this purpose natural variation among existing cultivars and conventional breeding can be used. On the other hand genetic engineering approaches such as RNA interference have also been applied.



Peter Koehler obtained his PhD from Technische Universität München on disulfide bonds of wheat gluten. Currently, he is vice director of the German Research Center for Food Chemistry in Freising, Germany. His research is focused on basic as well as applied topics from cereal science. Typical examples are studies on celiac disease, on structure and functional properties of wheat gluten and other cereal proteins as well as enzymes and emulsifiers in breadmaking. Since 1999 he has also been working as a professor for food chemistry at Technical University of Munich.

6. Enzymes

6.1. Tom Kleinhout, AE Leiden (The Netherlands)

Granular Starch Hydrolysing Enzymes for the production of glucose and maltose syrups

It has been known for decades that raw starch can be digested at sub-gelatinisation temperatures with the aid of enzymes. In 2005, DuPont Industrial Biosciences has developed the technology to go from corn or small grains directly into ethanol fermentation by using granular starch hydrolysing enzymes (STARGEN™ 002). But until now, the potential of using the concept of a low temperature process for carbohydrate processing has remained unexplored. This lecture will give an overview of our latest findings in the area of enzymatic granular starch hydrolysis. It will focus on the production of glucose and maltose syrups, both products being prevalent in the current sweetener industry.

The success of a ‘granular-starch-to-glucose-syrup’ production process is determined by several factors, primarily purity and solubility. The latter is mainly determined by the

dosage of alpha-amylase added to the mix of starch and water. The purity of the syrup is best achieved when limiting the reversion reaction while still ensuring fast conversion to glucose. The mix of gluco-amylase activity, alpha-amylase activity and debranching activity, results in syrup with more than 96% glucose and more than 97% solubility. This technology is robust as well: with stability across a broad pH and temperature range and the ability to handle dry solids content up to 40%.

In traditional production of maltose syrups one needs to apply alpha-amylase and beta-amylase separately. A low DE at the start of malto-saccharification is critical to reach high or very high maltose content (>60%). In our approach however we add both enzymes directly to the raw starch. This means that the exact ratio of alpha- vs. beta-amylase is crucial for reaching a high maltose concentration, and we found that the lower the dosage of alpha-amylase, the higher the maltose content will be (>80%). However, as the alpha-amylase is the driver for starch solubility, the balance is to be made between desired maltose percentage and expected solubility. With a clear understanding of how alpha- and beta-amylase and pullulanase cooperate in hydrolysis of raw starch, we believe this technology has high potential for the maltose market. Its deliverables (very high maltose >75% with acceptable solubility >75%) and robustness (broad pH and temperature range, with dry solids content up to 40%) only underline this conclusion.



Tom Kleinhout is an enthusiastic researcher who has been working for DuPont Industrial Biosciences for over three years now. His background is in Food Biotechnology in which he holds an MSc degree.

In his current role as Application Associate in Biorefineries he is involved with innovation projects and with technical service for customers in the 'bio-ethanol' and 'carbohydrate processing' business.

6.2. **Xiaoyuan Cui**, Franklinton (USA)

Low pH liquefaction with a new alpha amylase from Novozymes

In conventional starch conversion, caustic solution is added before liquefaction to bring the pH up from pH 4.0 to pH 5.8. And after liquefaction, the pH is reduced to 4.5 for saccharification to produce glucose syrup. This is simply because current alpha-amylase for liquefaction could not work at low pH range. The added chemicals need to be removed later in refinery process by ion exchange column, which is an expensive process. Recently, Novozymes launched LpHera®, a new alpha amylase enzyme that is designed to work for liquefaction at pH 4.5-4.8. LpHera not only reduces the use of pH-altering chemicals by more than 50%, but also yields 0.2% more dextrose in saccharification. The launch of LpHera starts a whole new era for low-pH liquefaction and offers starch processors the industry's lowest total cost of conversion.



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*Worked at National Starch & Chemical Company R&D department in
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working for National Starch.*

Has been working at Novozymes in Franklinton, North Carolina since March, 2008.

6.3. **Bart Koops**, AE Leiden (The Netherlands)

An improved Alpha amylase with fast viscosity reduction for starch liquefaction

Alpha amylases are widely used in the starch industry for liquefaction of starch at high temperatures. The alpha amylases are generally regarded as having random hydrolysis of the α -1,4 glycosidic bonds in starch. However, the alpha amylases are not entirely random and have a multiple attack action, which differs between different alpha amylases. Therefore, different alpha amylases have a different hydrolysis action which result in differences in performance.

In this presentation DuPont will present an alpha amylase, SPEZYME® ALPHA PF, that facilitates a very fast viscosity reduction in liquefaction. Due to the low viscosity, the enzyme can be used to process higher dry solid slurries, which has an economic and sustainability benefit.

The enzyme, SPEZYME® ALPHA PF, can be used to hydrolyse starch in a standard liquefaction process. A unique feature of this product is that it can be used in a wide pH range. The enzyme can be used to produce a high quality liquefact that when saccharified will result in good quality syrups. Any plant interested in testing this new product is welcomed to contact DuPont to collaboratively implement this in their liquefaction process.



Bart Koops is Director EMEA Biorefineries Applications at DuPont Industrial Biosciences. Bart studied biochemistry at the University of Utrecht in The Netherlands and obtained his PhD in enzymology at the same university in the Department of Enzymology and Protein Engineering in 1999.

Bart worked as Scientist at the R&D facility of Royal Numico in the Netherlands, and at Yakult as interim Science Manager and moved to the industrial biotechnology division Genencor within Danisco A/S in 2005.

After being responsible for technical sales for 6 years Bart moved to his current role in 2011 as EMEA Director Biorefineries Applications. He is leading the team in developing new products and processes for the grain processing industry and providing support for customers.

7. Sweeteners

7.1. **Michael Radeloff**, Berlin (Germany)

Polyols – more than sweeteners

Polyols – produced today at a millions of tons scale by hydrogenation or fermentation of carbohydrates from renewable raw materials – have become a valuable “natural” ingredient in a wide range of applications in the food, cosmetics, pharmaceutical, chemical and technical industry.

Polyols are saccharide derivatives in which the carbonyl group has been reduced to a hydroxyl group, therefore also named “sugar alcohols”. Production processes for polyols generally are based on high-pressure catalytic hydrogenation of the appropriate carbohydrates. Commercially available polyols extend from sorbitol, mannitol, maltitol, isomalt, xylitol, and lactitol to erythritol.

The traditional food use of sugar alcohols as low caloric sweeteners carrying a “sugar-free” claim often is combined with high intensity sweeteners to make up for the lower sweetness of sugar alcohols in comparison to sugar. The relative sweetness of polyols varies from less than half as sweet (lactitol 40%) to equally as sweet as sucrose (xylitol 100%). Despite the variance in food energy content of polyols, EU labelling requirements assign a blanket value of 2.4 kcal/g, a reduction of 40% compared to sucrose. Real values vary from 2.6 kcal/g for sorbitol to 1.6 kcal/g for mannitol and even 0.2 kcal/g for erythritol.

Sugar alcohols are slowly and incompletely absorbed into the blood stream. The resulting low glycemic index (GI) varies from 0 to 35 relative to pure glucose (GI = 100), which explains the interest for sugar alcohols in diabetic foods. However, sugar alcohols can cause diarrhoea therefore laxative warning is required for all foods containing more than 10% added polyols. As polyols are not fermentable by oral bacteria they do not contribute to tooth decay.

Other functional properties of polyols in food applications include a pleasant cool taste resulting from a negative heat of solution as strong as -43 cal/g for erythritol or mild as -6cal/ for maltitol. The physical, chemical and microbiological stability over a wide range of pH and temperatures but also crunchiness, compressibility, solubility, and hygroscopic properties providing humectancy, make them versatile and widely used ingredients in food products.

The worldwide consumption of polyols is estimated at close to 1.5 mio MT. More than half of worldwide production is used in food applications. However, about three quarters of sorbitol production is consumed by non-food applications. Thus sorbitol has become a bulk chemical introducing an element of sustainability in a world of petrochemicals. The manifold functionality of sorbitol beyond sweetness makes it a bulking agent, humectant, binder, complexing agent, plasticizer and chemical reactant. Thus it is an important starting material in the chemical production of ascorbic acid (vitamin C), for polyether polyols in polyurethane production, for sorbitan ester types of surfactants and for isosorbide derivatives. Sorbitol has become a chemical commodity competing successfully with other bulk chemicals such as natural glycerine, propylene glycol (PG) and polyethylene glycol (PEG).

The carbohydrate origin at improved chemical stability makes polyols and their derivatives valuable chemical building blocks whenever “green chemistry” solutions are intended.



Dr. Michael Radeloff. Consulting strength extends from use of renewable agricultural raw materials and production of derivatives across fields of application in range of markets. A chemist with international experience specialised in industrial business-to-business consulting studying markets, product needs and customer expectations addressing client product development requirements, training, marketing and communication strategies, production set-up, regulatory and quality assurance standards for sustainable products.

Thursday, April 10th 2014 (continued from page 2)

- 3.6. **Andreas Blennow**, Frederiksberg C (Denmark)
Engineering an amylose-only cereal starch

4. Green Chemistry

- 4.1. **Robin D. Rogers**, Tuscaloosa (USA)
Advanced Materials from Renewable Polymers: Why Are We Still Using Synthetics?
- 4.2. **Tatiana Budtova**, Sophia Antipolis (France)
A new approach towards starch granules: flavour perception and controlled release applications

5. Application

- 5.1. **Tamara Dapčević Hadnađev** and **Miroslav Hadnađev**, Novi Sad (Serbia)
Stabilized starches as bread improvers

12³⁰ – 13³⁰ Lunch Break

- 5.2. **Evžen Šárka, Petra Smrčková, Meltem Saglamtas** and **Jaroslav Koláček**, Praha (Czech Republic)
Influences on digestibility of corn grits during extrusion – process parameters, native or modified starch addition
- 5.3. **Maurice Essers, Susann Bellmann, Rob Havenaar** and **Ted Slaghek**, AJ Zeist (The Netherlands)
Amylose as an alternative dietary fiber
- 5.4. **Peter Köhler**, Freising (Germany)
Wheat Intolerances – Reasons, Consequences and Alternatives

6. Enzymes

- 6.1. **Tom Kleinhout**, AE Leiden (The Netherlands)
Utilizing Granular Starch Hydrolysing Enzymes for the production of Glucose and Maltose syrups

15³⁰ Coffee Break

- 6.2. **Xiaoyuan Cui**, Franklinton (USA)
Low pH liquefaction with a new alpha amylase from Novozymes
- 6.3. **Bart Koops**, AE Leiden (The Netherlands)
An improved Alpha amylase with fast viscosity reduction for starch liquefaction

7. Sweeteners

- 7.1. **Michael Radeloff**, Berlin (Germany)
Polyols – more than sweeteners

- 17³⁰** **Closing remarks** by the Chairman of the Starch Experts Group,
Willi Witt, Oelde (Germany)

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