

Review and Summaries

62. Starch Convention 2011

From the 13. till 14. of April, 2011 the Association of Cereal Research organized the 62. Starch Convention in Detmold. 197 participants from Austria, Belgium, Brasil, Canada, Denmark, France, Great Britain, India, Italy, Lithuania, Republik of Korea, Sweden, Switzerland, Taiwan, Thailand, The Netherlands, Turkey, Uganda, Phillipines, Uganda, USA and Germany visited this international well known congress. Lecturers from scientific and economic areas presented different interesting papers.

1. Introductory Lecture

1.1 **Alexander Jess**, Berlin (Germany) Current Developments in the Starch Market

The AAF – “Association des Amidonniers et Feculiers” - is the trade association which represents the interests of the European starch industry both at European and international level.



The European starch industry is a sophisticated and innovative industry that plays as a first processor industry an essential role between on the one hand, the EU agricultural sector, due to its significant consumption of EU-grown cereals and starch potatoes and on the other hand, a wide variety of industrial sectors as its starch products are used as ingredients, functional products and intermediates in food, feed and non-

food applications. Based on its experience of the last 30 years, it also has great potential in developing innovative bio-based products and will constructively contribute towards the establishment of a low-carbon, knowledge-bio-based economy of the future.

Therefore, the AAF is pleased to present its views on key EU issues of direct relevance to its competitiveness e.g. the sugar regime in the framework of the current debate on the Common Agricultural Policy towards 2020, the great potential for green chemistry developments, and a specific case study on paper and board.

2. Fundamentals

2.1. **Robert G. Gilbert**, Queensland (Australia) Starches with improved functional properties

The functional properties of both native and modified starches are controlled by the complex branching structure of individual starch molecules, as well as higher-level structural features such as degree of crystallinity and grain structure.



Improved functional properties therefore need causal relations between (i) biosynthesis, which controls native starch structure (discussed in the talk by AC Wu later in the program), (ii) changes in structure caused by any chemical, enzymatic or mechanical modification, (iii) how starch structure controls functional properties. Some examples of functional properties that are controlled by relatively simple structural features are

that (a) starches with longer branches ('high amylose' starches) are digested more slowly by humans, with nutritional benefits; (b) starches with large molecular sizes have higher solution viscosities.

The first need for elucidating the relation between biosynthesis, processing, structure and functional properties is proper structural characterization in a way that is as complete as

possible and does not degrade the analyte. Methods for obtaining one- and two dimensional distributions for the number, weight, average weight and branch length, all as functions of molecular size, and new methods for measuring overall molecular weight, branching fraction and degree of substitution, will be reviewed.

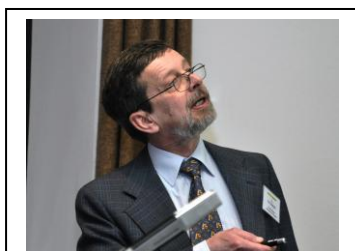
Mechanistic understanding of the changes in structure of starch as a result of processing and digestion comes from examining the evolution of these various size distributions (and other structural characteristics) during the course of the process. For example, starch extrusion is found to result in preferential cleavage of longer chains, and leads to amylopectin molecules being eventually broken down to a limiting size range which is commensurate with that of amylose; amylose in turn is not significantly degraded. Preferential scission of longer chains is also seen in wet-milling, which has nutritional implications, since longer chains are nutritionally beneficial. Moreover, while increased milling increases the amounts of cold- and hot-water-soluble starch, the size distributions show that this is due not only to molecular degradation but also to damage to higher-level structural characteristics. Examining changes in starch size distributions of model starch-based foods during *in vitro* and *in vivo* digestion shows many similarities but some distinct differences: the best current *in vitro* procedures, compared to corresponding *in vivo* pig studies, miss out some important qualitative effects in the evolution of the amylopectin component. Digestion studies on starch-containing foods show progression from cases where enzymatic breakdown is diffusion-controlled (especially applicable to lightly processed grains) through to following homogeneous (Michaelis-Menten) kinetics, applicable to well-cooked rice.

Each of these results can be understood in mechanistic terms. These types of studies, especially the mechanistic understanding they engender, have considerable potential for starch-based industries to choose starches and design processes with improved end-use properties.

2.2. Eric Bertoft, Guelph (Canada)

Recent Views on the Molecular Organization of the Semi-crystalline Starch Structure

Though starch granules vary widely in size and shape in different plants, they appear to have a remarkable similar internal architecture. Thus, alternating amorphous and semi-



Eric Bertoft

crystalline granular rings consist of ball-shaped "blocklets" with approximate diameters between 30 nm to a few hundred nm observed by atomic force microscopy. Small angle X-ray scattering techniques have shown that the semi-crystalline rings are organized into alternating crystalline and amorphous lamellae with a universal repeat distance of approximately 9 nm. However, the exact relation between "blocklets" and the stacks of lamellae remains obscure.

It is the major starch component, amylopectin, which forms the semi-crystalline rings. The comparatively short chains of amylopectin are organized into clusters and the external segments form double helices that crystallise into either A- or B-type allomorphs. Pérez and co-workers clarified the detailed organization of the double helices already more than 20 years ago. In contrast, virtually nothing was known about the molecular organization of the amorphous lamellae until recently. The amorphous lamellae consist of the extensively branched part of the clusters together with intercluster chain segments. These parts of the amylopectin macromolecule have been the focus of our work and it is now known that the branches of the clusters are organized into very small structural units named building blocks. A majority of the blocks consist of only 2–4 chains, but larger blocks with increasing number of chains up to the order of 10 exist in small amounts depending on plant source. The internal chain length (ICL) inside building blocks is only 1–3 glucosyl residues, whereas between the blocks ICL is in the order of 6–8 residues. Interestingly, these experimental numbers largely coincide with theoretical values derived by molecular modelling of parallel double helices resulting in the A- and/or B-allomorphs, as shown by

O'Sullivan and Pérez. Isolated clusters possess groups of chains that most probably are involved in the interconnection of two and increasing numbers of building blocks. This systematically results in comparatively long chains that generally are found in isolated clusters. These long chains are possibly also involved in the interconnection of the clusters and are suggested to form a backbone structure of the entire amylopectin macromolecule. In extension, this has far-going consequences on how the amylopectin component might build up the semi-crystalline structure in the starch granules.

2.3. **Alex Chi Wu**, Queensland (Australia)

Understanding the Genetics-Structure-Property Relations of Starch from Mutant Plants

The complex branched structure of starch influences its industrial and nutritional end-use properties. The structure of a native starch (and thus the structure resulting from any subsequent modification), is controlled by the biosynthetic processes in the growing plant. Present methods to control this process, e.g. by knock-out mutants to give starches with more long chains, are qualitative. This work gives the first quantitative model for the lengths of starch branches (the chain-length distribution, CLD) based on the underlying enzymatic activities: starch synthases, starch branching enzymes and starch debranching enzymes. The model fits a vast range of literature CLD data, and moreover reveals a structural feature which had never been noticed before but which can be readily distinguished in published data. Treating mutant CLD data with the model shows the expected trends (e.g. branching enzyme knock-out resulted in lowering of the branching activity as predicted by the model). This provides a new way to elucidate the effects of mutations in a quantitative manner. This model shows that enzyme activities in mutations which can result in a viable plant are quite restricted: mutations not obeying these restrictions would lead to amylopectin with CLDs unable to form the crystalline lamellae which give compact energy storage for the plant. This shows why efforts to create plants with very different CLDs (e.g. longer branches for slower digestion and more resistant starch) have had limited success. The model suggests a possible workaround to develop plants with structurally desirable starch by changing the binding specificity of starch synthesis enzymes through targeted mutagenesis.



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2.4 **Sylvia Radosta, Waltraud Vorwerg and Michael Geiger**, Golm (Germany)

Properties of Different Waxy Starches

Waxy starches or high amylopectin starches consist mainly of amylopectin molecules, giving that starch type different properties compared to normal amylose containing starches. Waxy mutants are known from corn, sorghum, rice, wheat, barley, potato and others. Waxy corn starch was grown on a commercial scale for many years and in recent years waxy potato starch came to the market. In this lecture the properties of waxy corn starch, waxy potato starch from breeding and waxy potato starch from genetic modification will be compared with normal corn and potato starch.



Looking at the isolated starch granules there is no clear difference in the appearance or granule size distribution of normal and waxy starches from the same plant species. The weight average molar mass of the waxy starches was in the same order of magnitude as that for the normal starches.

Looking at the amylopectin structure the amylopectin branch chain length of the waxy starches was comparable with normal starches for the A-chains and slightly shorter for the B-chains. The waxy starches started swelling at a lower temperature than normal starches and developed higher peak viscosity. At temperatures below 100°C more amylopectin was

dissolved from the waxy starches than from the normal starches. The concentrated solutions of waxy starches did not gel and showed no change of the storage and loss moduli during storage at 5°C. The solutions of waxy starches were viscosity stable during five freeze-thaw-cycles. The solutions from waxy-potato starch exhibited higher transparency during the first freeze thaw cycle compared to waxy corn starch. The solution from waxy corn starch were more turbid directly after preparation and after freeze thaw cycles but tolerated three freeze thaw cycles without phase separation.

3. Basics in Starch Technology – Enzymes/Plant design

3.1. Ronny Vercauteren, Vilvoorde (Belgium) Enzyme Technology in Starch Processing

An overview will be given on the current status of enzyme applications in the field of starch



processing. Both wheat and corn based processes will be addressed, with focus on the wheat area. The use of enzymes in the domains of steeping, syrup filtration, wheat-gluten separation and corn gluten filtration will be covered. Also the use of enzymes for the production of hydrolysed starchy products will be highlighted. This presentation gives an introduction to the following presentations.

3.2. David Kroese, Leiden (The Netherlands) Enzymes in Corn Gluten Filtration

As demand for many products produced from the traditional corn wet milling process has remained high recently, due in part to high world sugar prices, many plants are required to run at or above design capacity levels. High throughput in turn places demands for



maximum rates on processing equipment throughout the wet mill and syrup refinery process. One of these unit operations, the separation of corn gluten from gluten slurry with a rotary drum vacuum belt filter, can achieve improved performance with the addition of enzyme to the feed stream. A proprietary enzyme product, OPTIFLOW™ RC 2.0, which is a complex cellulase enzyme preparation produced in a controlled fermentation of *Trichoderma reesei*, is a combination of enzymes which modifies and hydrolyzes non-starch

carbohydrates. Treatment of the gluten slurry with OPTIFLOW™ RC 2.0 prior to filtration has been shown to significantly improve filtration rate, reduce steam usage in the subsequent drying step and improve the handling characteristics of the gluten product of the separation step.

3.3. Ralf Neumann and Dirk Haemke, Darmstadt (Germany) New Lysophospholipase for Glucose Syrup Filtration



The enzyme choice for the production of starch hydrolysates basically depends on the feedstock. Corn processing basically requires an α -amylase and a glucoamylase. Wheat is more difficult to handle, due to precipitants formed during the process prior to filtration. Debranching and so called "speciality" enzymes are common tools to increase the filtration rate of wheat starch hydrolysates.

AB Enzymes offers a couple of enzymes for the wheat starch

processing treatment. Besides (hemi)cellulases, a lysophospholipase has been launched on the market.

ROHALASE[®] F the lysophospholipase's trade name is derived from Trichoderma and as such a completely new molecule in the AB range.

ROHALASE[®] F hydrolyses lysophospholipids, thereby forming free fatty acid and glycerophosphatide. With the removal of the fatty acid, the emulsifying ability of lysophospholipids is destroyed and the filterability and clarity of hydrolysed starch syrups is improved.

3.4. Frank Taetz, Oelde (Germany)

Flexible Plant Design for High Value Side Stream Products

World market demand and price for raw products as well as final end products within starch, protein and biofuel industries are highly volatile throughout years now. Pricing is also driven by harvest yield, product availability and political influence.



Business model for existing and upcoming plant design therefore depends very much on product diversity/flexibility. Furthermore focus on high value side stream products becomes essential for overall plant performance and added value. High plant yield by optimized equipment reducing product losses is another key for success.

Market tendencies and specific approach will be shown on selected examples.

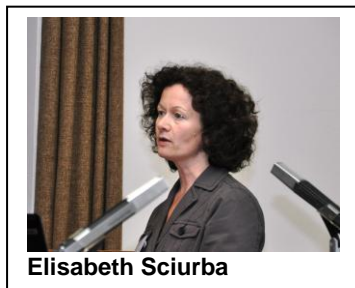
4. Raw Materials

4.1. Elisabeth Scieurba, Peer Figge, Norbert U. Haase and Meinolf G.Lindhauer,

Detmold (Germany)

Rapid Estimation of Wheat Quality for Starch Extraction – Challenges and Limitations

Wheat starch industry wants to process raw material with a special quality profile. In a research project we have developed near infrared spectroscopy (NIRS) models to give plant breeders access to these processing qualities on tiny amounts of grain.



Wheat samples from three consecutive growing seasons (2007 – 2009) were examined. They differed in quality (German wheat classification scheme E, A, B, and C), growing location, and nitrogen fertilization (extensive vs. intensive).

A comprehensive quality characterization was carried out at meal and flour (German classification type 550 with 0.55% mineral content). Focus was given on protein content, protein quality, volume ratio of large and small starch kernels, and the arabinoxylan content. Further on, even the characteristics of falling number, grain hardness, starch damage, and rheological behaviour were determined. The data obtained were subjected to statistical analysis to calculate significant differences between varieties and growing locations.

Near infrared spectra (NIR) of all samples were analyzed for each trait with a modified PLS (partial least squares) procedure reflecting to the whole wavelength range (400 – 2,500 nm). Internal validation and a scatter correction of the spectra (standard normal variate (SNV) and detrend procedure) were used. Original (OD [Log 1/R]) spectra, first derivative [$d^1(\log 1/R)$] and second derivative [$d^2(\log 1/R)$] spectra with gaps of 8 nm between two data points were tested for developing calibration models.

Next to protein, moisture, and grain hardness, for which NIRS models have already been described in the literature, it was possible to predict wet gluten, starch damage, and

gliadin and glutenin with coefficients of determination of 90%, whereas Zeleny index, starch content, the ratio of gliadin to glutenin and the ratio of large to small starch kernels could be predicted with less reliability (coefficient of determination 80 – 90%). Finally, the rheological properties and the arabinoxylane content could not be estimated sufficiently by NIRS method.

Summarizing the results, most of tested characteristics could be precisely predicted with the new developed NIRS models. This offers the chance for wheat breeders and for quality control at the factories entrance to improve or to check the quality profiles of wheat samples to be intended for starch processing.

5.1. **Salomeh Ahmadi-Abhari**, **Albert J.J. Woortman**, Groningen (The Netherlands), **Rob J. Hamer**, Vlaardingen (The Netherlands), **Katja Loos**, Groningen (The Netherlands) and **Lizette A.A.C. Oudhuis**, Zeist (The Netherlands)

Influence of Lysophosphatidylcholine (LPC) on gelation of diluted starch suspension and its effect on starch digestibility

Starch is the most common storage carbohydrate in plants and also the largest source of carbohydrates in human food. Starch is a key component of staple foods like wheat, rice



Salomeh Ahmadi-Abhari

and potato. In addition, starch has been widely used in food products not only as a main component but also to modify texture, improve moisture retention, control water mobility and maintain overall product quality during storage. Starch and starchy food products can be classified according to their digestibility, which is generally characterized by the rate and the duration of glycemic response. The starch in staple foods has been implicated in the complications related to obesity, type II diabetes etc. Enzymatic digestion of starch results in glucose

and its rate of digestion is considerably important. A slow rate is considered positive since this leads to lower metabolic stress. Predicting and controlling the glucose absorption due to ingestion of starchy food is of great interest in the context of worldwide health concerns.

Because wheat starch is a basic ingredient of so many foods, it formed the core of the present work to study the factors influencing the rate of starch digestion.

This study is a close look how to combine functional and structuring properties of wheat starch with its slower digestibility. For this we studied starch-LPC interaction in great detail. LPC, in the category of phospholipids, is widely used in food industries mostly as an emulsifier. Depending on LPC concentration, behavior of starch granules such as viscosity, granular shape and thermal properties while heating differs.

The effect of LPC on thermal properties and viscosity behavior of starch suspensions were studied using DSC and RVA respectively. The influence on granular shape was observed by light microscopy.

LPC at high concentration blocks functioning properties of starch, however its addition at low concentrations postpones pasting times and alters peak and end viscosities. In addition, swelling and solubility were hindered by LPC although they obviously increase due to heating and water ingress in absence of LPC. DSC results imply inclusion complex formation of LPC into amylose.



Kommer Brunt

5.2. **Kommer Brunt**, Heerenveen (The Netherlands)
Resistant Starch: Starch and Dietary Fibre Connected

Starches can be categorized amongst others according to their biological origin. The major starch crops are cereal starches as wheat, corn and rice and tuber and root starches as potato and tapioca. However starches can also be subdivided based on other, more physiological characteristics. Independently of the botanical origin, starches can also be subdivided between

native starch, damaged starch, gelatinized starch and resistant starch. From chemical viewpoint these starches are identical; however they differ significantly in physical, biochemical and/or physiological properties. These different categories of starches have different fields of application, e.g. amount of damaged starch in flour is an important quality factor for dough in bakery industry, the degree of starch gelatinization is important in pet foods and resistant starch is a dietary fibre constituent.

With different analytical methods it is possible to distinguish between these different starch categories. The different (enzymatic) methods of analyses for these different starch categories will be discussed.

Nowadays resistant starch is well recognized as an interesting dietary fibre constituent in our food. But the classical AOAC 985.29 and AOAC 991.43 analytical methods for the dietary fibre analyses are less suitable for the determination of resistant starch in food and food ingredients. Only the RS3 category of resistant starch is “seen” by these classical AOAC methods, and the categories RS1, RS2 and RS4 are not “seen”. Also these classical methods are inadequate for the quantization of low molar weight dietary fibres (prebiotics).

Presently there is a new AOAC 2009.01 method available for the total dietary fibre content, including all categories of resistant starch and the different prebiotics. The consequence is that applying this new AOAC method for the determination of the total dietary fibre content often results in a higher established dietary fibre content in the investigated sample than applying the classical AOAC 985.29 analysis. As an example the results of the established dietary fibre contents in bread applying both the classical AOAC 985.29 and the new AOAC 2009.01 will be presented.

5.3. **Christopher Mutungi**, Dresden (Germany) **Calvin Onyango**, Nairobi (Kenya),
Doris Jaros and **Harald Rohm**, Dresden (Germany)
Structural Characteristics of Enzyme Resistant Starch Type III: An Example of De-
branched and Hydrothermally Treated Cassava Starch

Microbiota residing in the human gut is integral to health, and the growth, metabolism, and viability are dependent on the nature of dietary components that escape digestion and absorption in the upper gut. Some forms of starch resist digestion due to structural reasons, and reach the lower gut where fermentation into metabolites that support health occurs. Short chain fatty acids, butyrate in particular, mediate the majority of health benefits. Recrystallized starch is a superior substrate for butyrate because of a structure that probably tilts fermentation pathways in favour of butyrate production.



Delivery of the health-benefits of resistant starch (RS) is possible through fortification of frequently consumed foods. To facilitate enrichment in a wide range of foods, industrial-scale production is enabled through conversion processes that have a high turnover of structurally stable preparations. Possibilities of enzyme mediated synthesis of RS from cassava starch were investigated. A high RS yield of above 80% is possible by hydrolysis of the α -D-(1 \rightarrow 6) branching points subsequent to gelatinisation, followed by hydrothermal stabilisation of the linearized polymers.

Structure of RS is important because it influences functionality and interaction with constituents of food systems where the starch is added as functional ingredient. Differential scanning calorimetry, X-ray diffraction, Fourier-transform infrared spectroscopy, Raman spectroscopy, and ^{13}C nuclear magnetic resonance were used for structural elucidation. Ordered and amorphous phases constitute structure of recrystallised starch; the ordered phase comprises crystalline and non-crystalline double- and single-helical polymers, and constrained conformations, depending on recrystallization method. This structural heterogeneity is responsible for a disparate

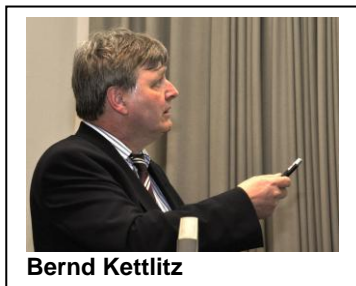
digestion resistance of different preparations. The stoichiometry of the conformations is bound to influence structure of the digestion residues, as well as techno-functional properties of the starch.

6. Food and Pharmaceutical Application

6.1. **Bernd Kettlitz**, Vilvoorde (Belgium)

Versatile Use of Emulsifying Starches in Food Applications

Development and production of affordable food products, with high and constant quality, are today the main drivers of all food manufacturers. Cargill anticipated these needs by developing a range of emulsifying starches, based on a natural and renewable raw material.



Bernd Kettlitz

Typical food ingredients, like egg yolk, Na-caseinate, and gum Arabic can easily be replaced by emulsifying starches, resulting in stable final goods. Emulsifying starches are successfully applied in dressings, creamers, beverage emulsions and encapsulated food ingredients and additives. In all these applications the n-Osa substitution will provide the emulsification properties. A new generation product has been developed by combining the n-Osa substitution with the mild treatment: bleaching, resulting in a stabilized product, when applied in a UHT process. Product will not contribute to viscosity development during the UHT treatment, but will develop full viscosity during final preparation at normal cooking temperature.

Manufacturers and customers will benefit from affordable solutions with constant quality.

6.2. **Lizette A.A.C. Oudhuis, Ricardo M.A. Nagtegaal, Therese Maarschalkerweerd, Jerry van Maanen and Maurice Essers**, Zeist (The Netherlands)

The Expanded World of Snacks – the Effect of Starch, Pregelatinized Starch and Water

The last years, there is a large tendency to develop (new) products with health-promoting ingredients such as lower salt or fat content or introducing fibers. Adding or replacing ingredients by more healthy ones is not easy, because the textural and sensorial properties of the product will change. The basic questions of our research are 1) what is the influence on changing the ingredients in indirect expanded snacks products on their expansion and texture and 2) how can these results be used to introduce healthy components or reduce salt and fat content to overcome the unwanted properties, such as bad expansion and texture.



Lizette A.A.C. Oudhuis

An indirect expanded snack is produced in two steps. First, a mixture containing potato starch, pregelatinized potato starch, water and salts is extruded at moderate temperature under such conditions that expansion does not occur. Secondly, the formed extrudates or pellets are expanded by deep-fat frying at 180°C. The focus of this presentation will be on the influence of different pregelatinized potato starches and water content of the extrudates on expansion and texture of snacks products. The techniques which are used are imaging, (modulated) DSC, DMTA, microscopy and SEM.

6.3. **Thomas Kipping and Hubert Rein**, Bonn (Germany)

Development of a Continuous Process for Producing Extrudets

Right now hot-melt extrusion is gaining more and more interest in pharmaceutical industry. One of the main advantages, apart from improving the bioavailability of an API, is the possibility to establish a continuous production line. The major problem right now is giving

shape to the final products. There are several different approaches for manufacturing solid dosage forms by extrusion. Some of them are already successfully established on the market, like for example calendaring or pelletizing.



Thomas Kipping

The main aspect of this work involves the implementation of a dynamic fly-knife cutting machine type Dynamat 60 from Metzner (Neu Ulm, Germany) into the production line. This sort of machine is widely used in plastics industry for cutting of cables and wires. A co-rotating twin-screw extruder type ZSE 27 HPPH from Leistritz (Nürnberg, Germany) was used for melting the material. Five different types of starch were used as basic substances. Phenazone and lidocaine were chosen as model substances. The melt was shaped by a round nozzle

with an internal diameter of 5 mm into endless strands. After a short period of cooling in a slope, the strands enter a belt feeder, which transports the material to the desired position. Mainly there are two different configurations for influencing the cutting process: Continuous mode and stop-and-go cut. The continuous mode provides a high throughput of material (up to 2000 cuts per minute) but cannot reach the high accuracy of the stop-and-go cut concerning cutting edge and cutting angle. For our tested materials it could be shown, that this process is also suitable for long-term operation. Blunting and clogging effects turned out to be much lower than expected.

This new technique opens up a vast field of application. Apart from manufacturing extrudets it is also possible to produce thin-layer muco-adhesive films, or implants.

The extrudets were analyzed concerning uniformity of mass, tensile strength, glass transition temperature and crystallinity.

7. Modification and Product Properties

7.1. Moo-Yeol Baik, Yonging (Korea)

Application of Ultra High Pressure Processing in Starch Modification

Ultra high pressure (UHP) processing is an attractive non-thermal technique for the food treatment and preservation at room temperature, and of great concern because of its potential to achieve interesting functional effects. The majority of the UHP process



Moo-Yeol Baik

applications on food systems have focused on shelf-life extension associated with non-thermal sterilization and reduction or boost of enzyme activity; only a few studies investigated modification of structural characteristic and/or functionality of proteins. Despite the rapid expansion of UHP application to food systems, limited information is available on effects of UHP on structural and physicochemical properties of starch and/or its chemical derivatives included in most processed foods as major ingredients or minor additives.

Therefore, functional roles of UHP in acid-hydrolysis, hydroxypropylation, acetylation, and cross-linking with POCl_3 and STMP/STPP reactions of starch granules, as well as physicochemical properties of UHP-assisted starch chemical derivatives were investigated. In case of UHP-assisted starch hydrolysis, corn starch with 2 N $\text{C}_2\text{H}_2\text{O}_4$ formed gel after UHP treatment, and corn starch with 2 N HCl showed partial destruction but corn starch with 2 N H_2SO_4 maintained its structure. Starch with 2 N HCl showed higher (42-47%) degree of hydrolysis compared to starch with 2 N $\text{C}_2\text{H}_2\text{O}_4$ (about 14%) and 2 N H_2SO_4 (13-14%) regardless of increasing starch content up to 20%. Therefore, UHP can be used for non-thermal starch hydrolysis and HCl would be a good catalyst for UHP starch hydrolysis compared to H_2SO_4 and $\text{C}_2\text{H}_2\text{O}_4$. Effects UHP level, pressing time and HCl concentration on UHP-assisted starch hydrolysis were also investigated. Corn starch granules maintained their structure up to 450 MPa and were partially disintegrated at 600 MPa. Degree of hydrolysis did not change up to 450 MPa and dramatically

increased at 600 MPa indicating that starch hydrolysis increased with increasing destruction of starch granules. Pressing time did not affect the degree of hydrolysis. On the other hand, degree of hydrolysis and destruction of starch granules increased with increasing HCl concentration up to 4 N. In case of UHP-hydroxypropylated corn starches, swelling power, solubility, RVA pasting properties were in the medium range between native and conventionally hydroxypropylated corn starches. On the other hand, UHP holding time (5, 15 and 25min) at 400MPa did not affect measured physicochemical properties. In case of UHP-acetylated corn starches, swelling power and solubility revealed higher value than native but lower than conventionally acetylated cornstarches and increased with increasing acetic anhydride concentration. UHP-acetylated corn starches showed distinctive RVA pasting properties compared to native and conventionally acetylated corn starches. UHP- acetylated corn starches showed relatively lower peak viscosity than both native and conventionally acetylated corn starches. In case of cross-linking with POCl_3 , both UHP and conventional methods revealed similar physicochemical properties. Therefore, UHP cross-linking with POCl_3 can reduce the reaction time from 120 min to 15 min. On the other hand, in case of cross-linking with STMP/STPP, swelling power, solubility and RVA pasting properties of UHP cross-linked corn starches were clearly different with conventionally cross-linked corn starches. UHP cross-linked corn starches with STMP/STPP revealed similar behaviors to substituted (i.e. phosphorylated) corn starch. Therefore, UHP can be used in starch modification and UHP-modified starches revealed similar or distinctive physicochemical properties compared to conventionally modified starches.

7.2. **Johannes W. Timmermans, Theodoor M. Slaghek, Jan M. Jetten and Ingrid K. Haaksman**, Zeist (The Netherlands) Superheated Steam Modification of Starch

Acylated derivatives of polysaccharides, in particular starch, are important materials since acylation introduces useful functionalities, such as decreased or increased hydro-philicity, ionic functions, coupling functions, crosslinking, etc. Acylation is conventionally performed by treating starch with an acylating agent such as



Johannes W. Timmermans

an acyl halide or an acid anhydride. These acylating agents are typically more expensive and less environment-friendly than the acids themselves. Moreover, these acylations result in a substantial amount of salt. The acid halides produce on a molar base more halide salt than the obtained degree of substitution.

Because an acid anhydride molecule can introduce at most 1 acyl substitution, even with an efficiency of 70% only one third of the acid is coupled to the starch. Moreover, using an anhydride the pH must be kept slightly alkaline which results in a less convenient process and a large amount of the salt of the carboxylic acid.

TNO has extended experience with superheated steam (SHS) processing of food and has patents on different SHS processes and products. Examples are alternatives for oil frying, reduction of acrylamide content and dissolution of biomass. In this project the chemical derivatization of starch was examined using super-heated steam.

There is a need for clean label food additives and the reduction of chemicals and used energy. To take account with these demands the acylation of starch using only unmodified carboxylic acids and starch was studied. This appeared possible using superheated steam, without the addition of other chemicals. Adipic acid was chosen as a model carboxylic acid. The superheated steam parameters were studied extensively. Thereby the temperature, reaction time and relative saturation of water was varied. This was done for different ratios of adipic acid and starch. The obtained degree of substitution and the efficiency with respect to the amount of used adipic acid was compared with the experimental conditions. A degree of substitution of 0.07 could be achieved and products were obtained in which more than 50% of the adipic acid was covalently bound. The water

content during processing appeared an important parameter. This makes SHS the method of choice as the water activity can be regulated fast and accurate. The obtained modified starches were still granular and could be washed with water to isolate the uncoupled adipic acid. As no modification of the carboxylic acid is needed and no other chemicals are used the uncoupled adipic acid can be recovered easily. Another advantage of the applicability of unmodified carboxylic acids as acylating agents is that a large variety is available, including food grade acids.

7.3. **Evzen Šárka**, Prague (Czech Republic)

Acetylated A and B Wheat Starches with Higher Degree of Substitution for Biodegradable Composites.

Wheat starch has two different types of granules, the so-called “A-starch” and “B-starch”, which are refined into two parts during starch processing. These types differ not only in a size or a shape but also in a chemical structure of amylopectin, its arrangement in a granule, content of lipids and proteins. Food application of wheat B-starch as a result of lower quality is problematic therefore the challenges for other using of B-starch have been taken up in designs of new technological processes.



Evzen Šárka

Starches having a degree of substitution (DS) of 0.01–0.2 are of commercial interest because of their usage esp. in food industry. The use of starch in biodegradable plastic materials seems to be perspective. Starch, however, suffers from a lack of moisture resistance and brittleness. Acetylation of the hydroxyl groups of starch to increase hydrophobicity is one approach toward increasing the water resistance.

The aim of our research project is to tailor mechanical behaviour, degradability and lifetime of biodegradable thermoplastic materials by incorporation of the B-starch. Therefore the suitable reaction conditions to receive the high acetylated starch were tested.

Wheat B-starch in native or pre-gelatinized form was acetylated using acetic anhydride and NaOH as a catalyst, at various reaction times for temperatures in the range of 115–128 °C. Degree of substitution was determined by measurement of ^1H NMR spectra and according to Wurzburg and compared with statistically analyzed data of FT-IR spectra. The kinetic constants for native and pregelatinized B-starches were calculated.

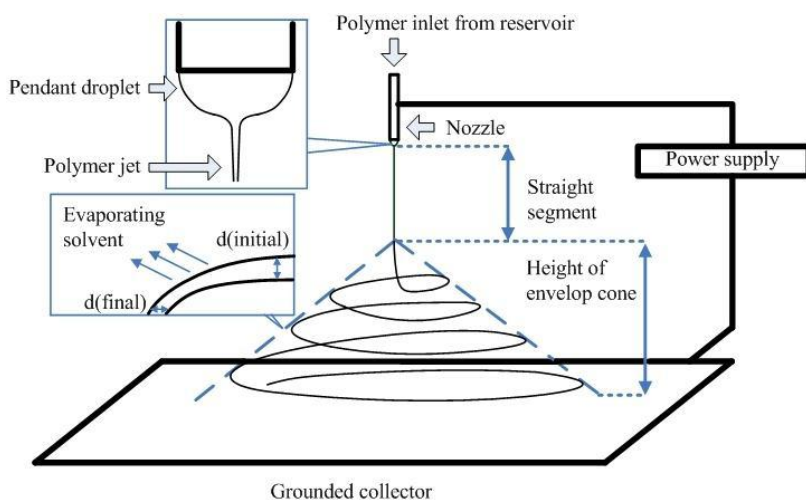
The following parameters of the dried and grinded product were studied: particle size measured by image analysis and laser diffraction, crystalline structure by X-ray diffraction pattern, temperature and enthalpy of gelatinization.

Native or pre-gelatinized wheat starches (A and B types) or acetylated derivatives of native starch with degree of substitution DS of 1.5 – 2.3 (10, 20, and 40 % m/m) were blended with poly-(ϵ -caprolactone) (PCL). Structure of the prepared films was analysed by FT-IR spectroscopy in comparing with the initial polymers. The following mechanical characteristics of prepared films were derived from the stress-strain curves: Young modulus, yield stress, stress-at-break and strain-at-break. Water absorption of PCL/starch (60/40) films was determined according to European standard ISO 62. The measured data were compared with those ones of commercial A-starch. The films containing native starch degraded in compost totally during 1-2 months. Acetylation of starch molecules in the composites reduced the degradation rate. Optical microscopy, in combination with the image analysis system NIS-Elements vs. 2.10 completed with an Extended Depth of Focus (EDF) module, was used to study the surface morphology of the PCL/starch films after 20-day and 42-day compost incubation. Chemical changes in the compost used for film exposition were measured.

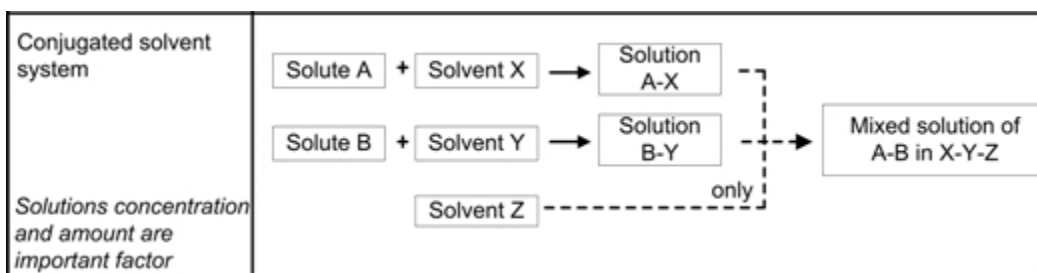
7.4. **Jackapon Sunthornvarabhas, Pathama Chatakanonda, Kuakoon Piyachomkwan and Klanarong Siroth**, Bangkok (Thailand)
Cassava-based Material in Medical and Packing Application



Cassava-based composite fibers were fabricated for skin tissue scaffold application. Novelty of electrospun cassava-based composite project is a method of solution preparation to achieve homogeneous solution from immiscible solution without using emulsifier or compatibilizer that is not applicable in this study.



Electrospinning Process Diagram

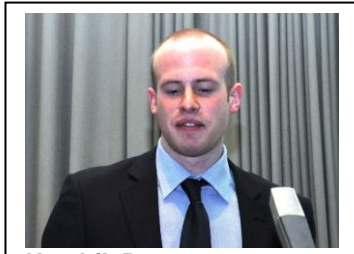


Conjugate solvent mixing scheme

Conjugated solvent was introduced during solution preparation between cassava starch indimethylsulfoxide solution (gelatinized starch) and Polylactic acid in dichloromethane solution and conjugated solvent which selection is based on intermediate polarity between 2 solvents of both solutes. Smoothed composite fibers with starch as solid content range from 5-40% were fabricated in a range of few hundred nanometers to a few microns by electrospinning process. Human and mouse fibroblast cells were proliferated at 100% viability on electrospun sheet composite between cassava starch and Polylactic acid.

7.5. **Hendrik Petersen, Sylvia Radosta and Waltraud Vorweg**, Golm (Germany)
Combinations of Cationic Starches with Synthetic Polymers in the Wet-end Process of Paper Production.

Cationic starch ethers are applied to the aqueous fiber suspension in the wet end of paper machine in order to increase the dry strength of the paper and the retention of fines and fibers. Depending on the raw material and the water quality as well as the favoured paper product, it is necessary to add more chemical additives to the wet end. With an FNR promoted project, the influences of additional cationic additives in relation to the adsorption behaviour of cationic starch derivatives and the resulting paper properties were investigated. The effect of starch origin and degree of substitution (DS) in combination with different synthetic cationic polymers, with regard to the adsorption on cellulosic fibers and the flocculation behaviour with anionic trash, was the aim of the investigation.



Hendrik Petersen

The determination of the adsorbed amounts was done indirectly by quantifying the polymers which were not adsorbed in the fiber suspension with GPC-MALLS. Symplex- and floc formation, occurring because of electrostatic interaction between cationic starch and anionic trash, were investigated with turbidity and particle analysis.

Adsorption studies in kraft pulp and filler containing pulp suspensions showed that cationic starch adsorption to the filler increased in water with rising conductivity.

Generally the presence of synthetic polymers decreased the starch adsorption manifestly. This effect was especially pronounced when polymers with high cationic surface charge, like PolyDADMAC, were applied to the fiber suspension. The competition during surface adsorption could be minimized when PolyDADMAC with comparatively small molecular weight ($M_w < 100$ kDa) was used. The dosage of the starch before the synthetic polymer decreased their negative effect, too. The adsorbed starch amount correlated well with the dry strength of produced handsheets. The Comparison of cationic potato starches with different DS and different starch origins pointed out that the potato starch with DS=0.065 was least affected by the presence of the synthetic polymers.

Anionic trash like lignosulfonate can affect the value of cationic additives. Turbidity measurements showed that the cationic potato starches caused a more major floc formation with lignosulfonate than cationic corn starch. This was because cationic potato starches produced a higher quantity of flocs in a bigger dimension.

The used methods provide the possibility to valuate specific interactions in different multicomponent systems. But because of the fact that every paper mill has a varying material composition and paper machine, it is not possible to forecast a universal dosage suggestion relating to these investigations. However the potential exists to analyze individual factors and thus make it easier to decide how to apply the additives.

7.6 **Enrico Pigorsch, Eckhard Möller and Birgit Kießler**, Heidenau (Germany),
Matthias Finger, Steffen Thiele and Eike Brunner, Dresden (Germany)
New Possibilities for the Analysis of Starch Distribution in the Paper Cross-Section by Raman Spectroscopy

Starch products are important additives in the paper industry. The purpose of the application of starch solutions or slurries on paper and paper board are, for example, to provide resistance to penetration of liquids, to give better surface properties and to increase internal strength. The resulting paper properties depend strongly on the starch penetration and its consequent cross-sectional distribution (z-direction) in the paper sheet. Therefore, it is important to know the z-distribution of starch in paper and paper board.



Enrico Pigorsch

Presently, the analysis of the z-distribution of starch in paper is mainly done by iodine staining of cross-sectional cuts and a following image analysis. Despite its proven practicability, this method has some drawbacks. It is an indirect method, the sample preparation is time consuming and in some cases the staining can be unspecific or difficult to detect. Therefore, an analysis method that is direct, faster and more specific is desirable.

Raman spectroscopy offers new opportunities to analyse the z-distribution of substances in paper, making it possible to selectively detect organic and inorganic chemical compounds. The use of an excitation laser and an optical microscope provides for a very high spatial resolution of up to 1 μm . Paper samples can be measured directly, i.e. there is no need for lengthy or complicated preparation procedures. To study the distribution of substances, spectra are acquired point by point across the entire cross-section of the paper. The data collected in the scanned area can then be used to generate spectral images and distribution curves.

Raman spectroscopy is particularly suitable for starch analysis because the numerous OH groups present in starch and also in cellulose give no signals in the Raman spectra. Therefore, unlike infrared and near infrared spectra, the Raman spectrum shows many other typical vibration bands of starch which can then be evaluated. Moreover, the signals generated by substituents can be easily identified in modified starches.

The lecture presents Raman spectroscopic studies for the analysis of the starch distribution along the paper cross-section. Several results obtained from model systems and real world paper samples will demonstrate the new possibilities for the visualisation and analysis of starch in paper and board by Raman spectroscopy.



Hermenau, Botterbrodt, Strandt



Kroggel, Pal



Team der AGF und der DIGeFa GmbH



Kröner, Witt, Bümmer

