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Prediction of Rheological and Chemical Properties of Different Starches Used in the Paper Industry by Near Infrared Spectroscopy (NIRS)

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Summary: Starch is one of the most abundant biopolymers, consisting of the polysaccharides amylose and amylopectin and other minor but characteristic constituents depending on the origin. Potatoes, maize, wheat, rice and tapioca are the sources of commercial interest with a large variety of applications both in food and non food areas. The measurements of over hundred starch samples were accomplished over a range of 4000–10000 cm^{-1} in diffuse reflectance and transmission mode. Quantitative prediction models, based on a partial least squares (PLS) algorithm for the determination of fat content, the main fatty acids, water content, tendency to retrogradation and viscosity were developed. All models are characterized by high correlation coefficients ($R^2 > 0{,}98$). Principal components analysis (PCA) was applied successfully to distinguish starches regarding their source, provenience and their degree of modification. Both quantitative and qualitative models are cross validated.

Keywords: biopolymers; fatty acids; near infrared spectroscopy (NIRS); rheology; starch

Introduction

Starch is one of the most abundant biopolymers, consisting of the polymers amylose and amylopectin and other minor constituents like water, phosphorus, proteins and lipids. Found as storage polysaccharide in plants it is accumulated as granules in various types of tissues and organs in a range between 65 and 90% of the total dry matter. Potatoes, maize, wheat, rice and tapioca are the sources of commercial interest with a large variety of applications both in food and non food areas, the latter being mainly paper- and textile industries. The possibility of numerous modifications, obtained in a physical, chemical or biochemical way and swelling, a characteristic property of starch, turns it to a highly used and appreciated raw material.[1]

As multifunctional and biodegradable ingredients starches are used to improve modern food and beverage processing. The systematic employment of starch plays a decisive role in baked goods, frozen foods, batters and breadings, beverage, emulsions and flavour encapsulation, confectionery, dairy products, fruit preparations, soups and sauces, dressings, meat products fat mimetics and savoury snacks.[2]

Starch and other biopolymers like guar or carboxymethylcellulose (CMC) will always be subjects to variations regarding their chemical composition depending first of all on the source, but also seasonal and geographical differences are readily identifiable. As the textural benefits of starch depend also on other components like bounded lipids, the selection of the matching starch for a complex food formulation and constant quality are very important. Viscosity is a guiding process control parameter of starch cooking or enzymatic

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degradation of starch slurries. Rapid methods of intake control and process control are therefore essential. Highly time-consuming standard methods for the determination of the chemical composition, physical properties as well as various impurities could be substituted by the implementation of in-line systems based on near infrared spectroscopy (NIRS). The aim of this work was the verification of the applicability of NIRS for the characterization of starch for industrial purposes.

Material and Methods

Commercial available biopolymers with their application fields in food as well as in non-food industry were received with thanks from Agrana GmbH (Austria), Cargill Inc. (USA), and Roquette (France). The reference analysis and the NIR measurements were done on native maize starch (95), native potato starch (20), modified potato starch (35), modified maize starch (4), tapioca starch (5), standards of modified potato starch (15), blends of native maize and potato starches (14), to extend the dataset and the and the field of application samples of guar (6) and CMC (20). The powdery samples were produced in Austria, Germany and France.

Near Infrared Spectroscopy (NIRS)

The near infrared spectroscopy measurements of the samples were carried out on a FT-NIR spectrometer Antaris I (Thermo Fisher Scientific, USA). Spectral acquisition was handled by means of the dedicated software, Result Version 2, ©Thermo Nicolet Corp.

For the determination of the chemical parameters fat and water content, fatty acid composition and the disposition to retrogradation, the spectra of the powdery polymer samples were measured in diffuse reflection using a spinning sample cup whereas each sample was replicated five times. 32 Scans were scanned in the full wavelength range of the instrument (4000–10000 cm^{-1}) with a resolution of 8 cm^{-1}.

For the determination of the physical parameter viscosity starch slurries were measured in transmission mode at 60 °C using a thermostatable cuvette holder. The respective background measurements were done in the measuring position once in an hour.

Techniques based on near infrared spectroscopy technology are known for fast and non-destructive analysis with high information content. Being a relative measuring procedure a comprehensive calibration based on an extensive set of reference data. The NIR models for the determination of the parameters referred to were done by multivariate data analysis.

Reference Methods

Water Content

The water content [%] of the single starch samples was determined thermo-gravimetrically using an infrared dryer (Mettler Toledo, Switzerland).1g of starch powder was dispersed on aluminium dishes and dried at 130 °C till weight consistency (2mg/30sec) was achieved.

Total Fat Content and Fatty Acid Composition

Fatty acids are incorporated in the helical structure of amylose which have to be released in a first step by acidic hydrolysis prior to extraction. The official standard method due to Weibull-Stoldt could be accelerated by the development of an "all-in-one-pot–technique" which allows hydroysis and extraction in only one reaction tube. To 2 g starch 0.2 mg triundecanoin (Larodan AB, Sweden) was added as internal standard. The hydrolysis was carried out in 40 ml vials with 10ml sulfuric acid (12%) at 80 °C for 30 minutes stirring constantly. At room temperature 4ml of n-heptane were added and the fatty acids were extracted for 10 min on a shaker (Vortex Genius 3, IKA®). An aliquot of the extract was transmethylated with methanolic sodium hydroxide at 80 °C for 30min followed by a derivatization step with bortrifluorid/methanol (80 °C for 15 min). The fatty acid methyl esters

(FAME) were extracted with n-heptane. The following gaschromatographic separation was carried out on a HP 5890 GC using a polar column (DB-Wax, 15 m · 0.25 mm · 0.25 μm). The injector temperature was set at 220 °C and that of the flame ionization detector (FID) at 260 °C. The oven temperature was held for 1 min at 50 °C and was risen with 15 °C/min to 140 °C and with 8 °C/min to 240 °C which was held for 5 min. The single fatty acids were identified by an external standard (GLC 68C, Nu-Chek Prep Inc., USA) and quantified by the internal standard.

Retrogradation

The characterizing phenomena of gelatinization and retrogradation of starch can be observed by differential scanning calorimetry (DSC) recording alterations of enthalpy.[3] Suspensions of starch powders (5 mg) and distilled water (10 μl) were equilibrated in hermetically sealed aluminium pans for one hour at room temperature prior to the DSC measurements performed on a Diamond DSC instrument (Perkin Elmer, USA). For the DSC analysis the sample and reference pans were heated by two independent furnaces starting from 20 °C to 95 °C with 10 °C/min. After the DSC run the sample were stored at room temperature for 10 days and measured again under the same conditions as at the first run. Retrogradation [%] was described as the ratio of the measured enthalpies of the first run to the second run.[4]

Viscosity

The viscosity of different pre-treated biopolymers was determined by rotation viscosimetry on a rheometer (MCR, Anton Paar Physica, Austria) equipped with a cone-plate (2°/75mm) system. As the case may be guar, CMC and starch samples of varying concentrations (0.05–5%) in distilled water underwent a hot or cold swelling procedure. The gelatinized samples (1.5ml) were transferred void-free to the preheated plate (60 °C) of the rheometer as well to culture tubes for the NIR measurements. The samples were measured applying shear rates from 10^2 to 10^{-3}. For the preparation of the flow curve (shear rate/strain rate against dynamic viscosity η') 60 data points were recorded. The constant initial viscosity η_0 [Pa.s] can be read off from these curves.

The NIR analyses in transmission and the rheological measurements were carried out simultaneously applying the same temperature conditions.

Each sample designed for the reference data set was measured at least twice.

Multivariate Data Analysis

NIR spectra are dominated by overlapping overtone and combination bands of −CH, −OH and −NH functionalities causing very low structural selectivity. Therefore multivariate data analysis for the calibration with reference data is required.[5]

The NIR calibrations of the single parameters based on a partial least squares (PLS) algorithm and qualitative analysis applying principal component analysis (PCA) were done using the software Unscrambler® 9.2. (CAMO, Norway). Prior to the calibration step the spectral data had to undergo pretreatments as multiple scatter correction (MSC) which is effective to correct scatter effects and to reduce the influence of particle size[6] and the standardized normalization procedure was applied to reduce the effect of a in general pronounced baseline drift in NIR raw data. The whole range (4000–10000 cm^{-1}) was used for the calibration. For the NIR models of the parameters retrogradation and viscosity the first derivative of the spectra was used. All models are cross validated.

Results and Discussion

NIRS is known as a very fast and non-destructive technique, once established a robust NIR calibration with the correspondent reference data for the requested parameters. The NIR calibration instead is a highly time-consuming procedure, as it requires a comprehensive and representative reference data set with a highly analytical claim for the reference methods, as the quality of a prediction NIR model stands and falls with its reference data. NIRS finds its application mainly in the industrial environment due to its possibility of an in-line implementation using fibre probes in incoming goods inspection and process control installations. Qualitative considerations of starches in quality control are of not less importance than quantitative ones. In industries, e.g. the paper industry, starches of different quality and origin are employed, which can be determined by NIRS within seconds applying based on PCA cluster models. The PCA plots shown in Figure 1 and Figure 2 demonstrate clearly the high potential of NIRS. Starches of different origin (maize, wheat, tapioca and potato) can be identified in a few seconds applying a classification based on SIMCA (Soft Independend Modeling of Class Analogy). Maize starches of different provenience (France and Austria), achieved at the same harvest time, could also be classified well, which points out the feasibility of NIR techniques (data not shown).

For the purposes of paper industry potato starch is higher appreciated than others because of little amounts of lipids and proteins compared to maize starch for instance.

In Figure 2 (above) the potential of PCA of a distinctive classification of native and modified starches is shown and also the blends (a–h) are illustrated clearly. Possible impurities of potato starches by maize starches (1–35%) can be determined quantitatively applying a PLS algorithm as shown above in the same figure.

As modern paper industries are running their processes already in nearly closed circuits it is important to apply well characterized raw material as their components will be accumulated in the process water. A well-known problem in paper industry is the accumulation of retrograded amylose particles (RAPS) in which fatty acids of starch are thought to be involved, as starch is used in high amounts. RAPS cause deposits in the tubings and on the

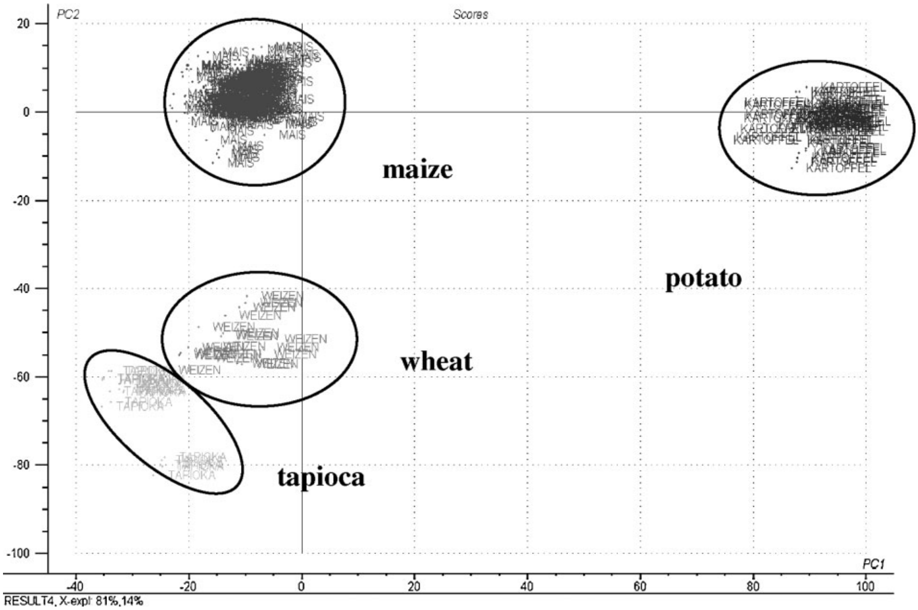

Figure 1.

PCA plot of different starches applied in paper industry (tapioca, wheat, maize and potato). The spectral data is recorded in diffuse reflectance.

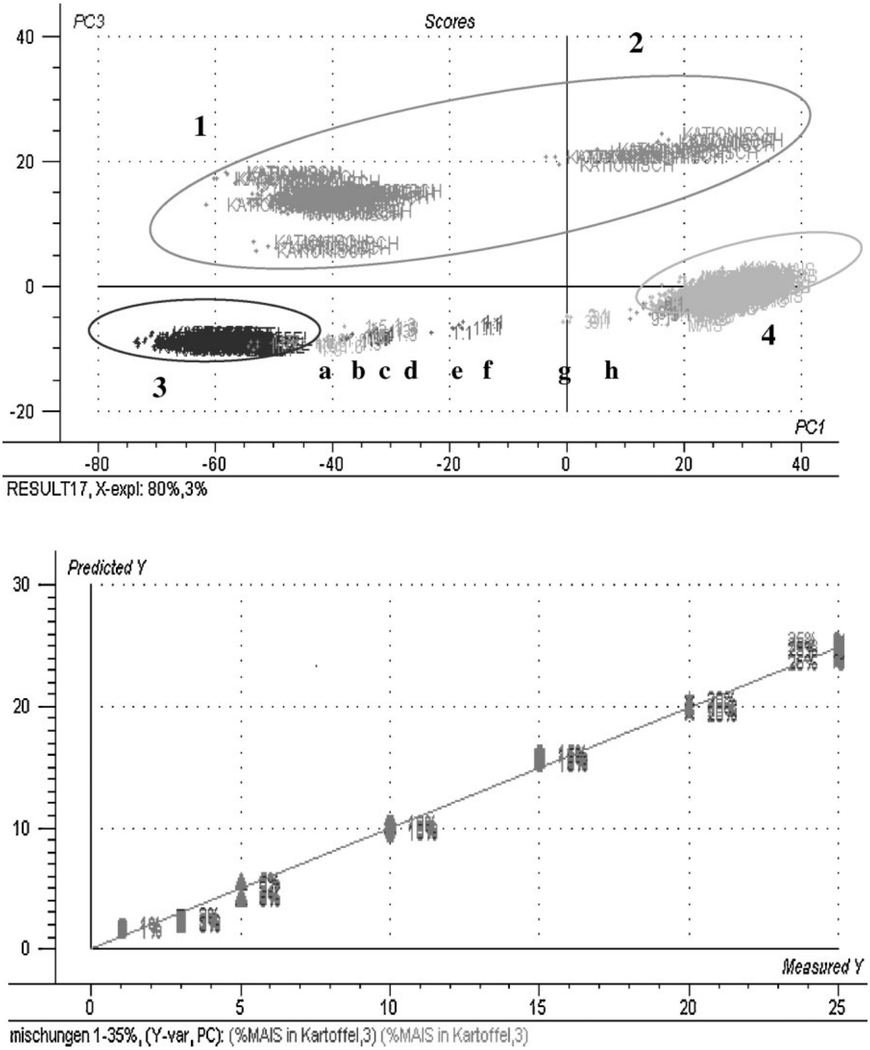

Figure 2.
above: PCA. The data set contain native potato (3) and maize (4) starches and the respective modified specimen (1, 2), as well blends of native potato and maize starches (a-h). *below:* PLS. Different concentrations (1-35%) of maize.

paper machine as well on the product itself which leads to a striking reduction of the paper quality and even to the point of process shut down. Therefore the determination of fat (fatty acids) is one of the most important chemical parameters in quality control. Official standard methods cannot satisfy the need of an efficient working quality control. All reference methods for the NIR calibrations are validated for the ranges of concern. In Table 1 an overview of the elaborated quantitative NIR models for the determination of the parameters of interest is given. NIRS has already turned to a standard procedure measuring fat, water and protein contents in food since intensive work done by Karl Norris in the 1970ies. In contrast to food analysis were lipids are considered as main constituents in starch they range between 0.6 and 8 mg/g. The main fatty acids detected in starches are palmitic acid (C16:0), stearic acid

Table 1.
Summary of the elaborated NIR models based on a PLS algorithm and their characterizing parameters.

Model	Samples	R^2	RMSEC	RMSEP	range
C16:0	115	0.991	0.084 mg/g	0.088 mg/g	0.5–1.7 mg/g
C18:0	115	0.988	0.005 mg/g	0.005 mg/g	0.06–0.1 mg/g
C18:1	115	0.980	0.045 mg/g	0.047 mg/g	0.2–0.7 mg/g
C18:2	115	0.989	0.13 mg/g	0.10 mg/g	0.8–2.6 mg/g
Fat	115	0.991	0.29 mg/g	0.29 mg/g	0.6–8 mg/g
Water	80	0.984	0.43%	0.44%	9–25%
Retrogradation	65	0.988	1.35%	1.39%	20–70%
Viscosity	50	0.997	2.64Pa.s	4.22Pa.s	1–300Pa.s

(C18:0), oleic acid (C18:1) and linoleic acid (18:2).

The calibration set for the parameters fat and fatty acids comprises 115 starch samples and 575 spectra; in Figure 3 the raw spectra of tapioca, wheat, maize and potato starches is shown. Prior to quantitative analysis a MSC procedure was applied to the spectral data used for the prediction of the mentioned parameters. Based on these spectra, quantitative PLS models with 3 factors (fatty acids) and 2 factors (total fat) were developed. The validated methods show high precision and reproducibility with low root mean square errors of calibration (RMSEC) and low root mean square errors of prediction (see Table 1) and correlation coefficients R^2 between 0.980 and 0.991.

The water content of starches could be modeled with 4 factors to achieve robust prediction models with a RMSEC of 0.43%, a RMSEP of 0.44% and a correlation coefficient of 0.984. Adding guar and CMC samples to the calibration set, the model parameters did not alter significantly ($R^2 = 0.973$).

In the case of the PLS models of the physical parameters retrogradation and viscosity a data pre-treatment in form of a 1st derivative was needed. Using 8 factors respectively high correlation factors could be obtained (>0.988), showing low RMSEP each. For the PLS models of viscosity 250

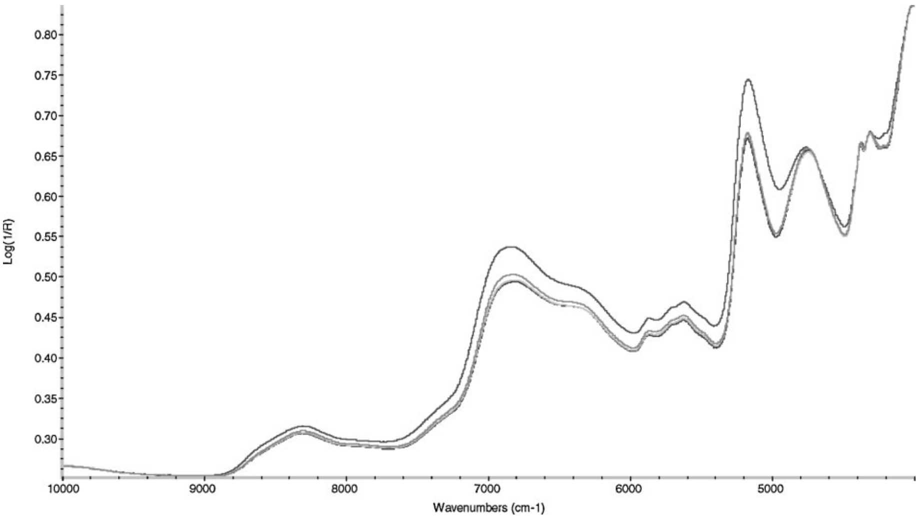

Figure 3.
Raw spectra of wheat, maize, tapioca and potato starches, obtained in diffuse reflectance.

spectra of 50 samples were collected in transmission mode.

The high molecular starch has to undergo a cooking procedure or an enzymatic degradation before its application. The progression of starch degradation is characterized by a decrease of viscosity. In paper and food industries viscosity is considered as an important parameter in process control and is routinely measured to assure texture properties. The possibility of employing near infrared spectroscopy is reported recently. [7,8]

Gelatinization and retrogradation are characteristic phenomena associated with starch. Gelatinization occurs when starch is heated in the presence of enough water and starch granules swell losing their crystalline structure to form amorphous regions and leaching amylose.[9] Retrogradation means an aggregation and re-crystallization of the amorphous region in gelatinized starch, when kept below the gelatinization temperature. The process consists of a rapid gelation of amylose, solubilized during gelatinization and a slower re-crystallization of amylopectin. Gelatinization is an endothermic process which can be recorded by DSC measurements.[10] Starches show different structures (A-type and B-type) and different amylopectin chain-length distributions depending on their origin, which is reflected in their retrogradation behavior. Retrogradation can be modeled as described above and estimated by DSC measurements resulting in precise NIR prediction models, when used as reference method. In practical applications the estimation of the tendency of retrogradation for a specific batch will be more interesting than exact values. We could show that NIRS is able to satisfy these requirements.

Conclusion

Standard reference methods (up to 10h) cannot comply with the requirements of modern quality control. Near Infrared Spectroscopy is a promising, very fast (30sec) alternative technique which provides in combination with chemometric methods qualitative and quantitative information. Classification of unknown samples as well the determination of impurities and chemical properties (e.g. fat, fatty acids, protein, water) can be done in-line as well as at- or on-line. The acquisition of NIR spectra of starch in the incoming goods inspection allows the identification of problematic starch batches before its processing. The possibility of the determination of many parameters simultaneously and in-line by recording a single spectrum compensates for the time consuming calibration step. As there are in-line viscosimeters available on the market the implementation of NIRS for monitoring the rheological behavior of starch slurries in papermaking is thought to be a yet another application of an already existing NIR in-line installation. NIRS proved its applicability in the industrial quality control for the parameter of interest, substituting time-consuming standard methods.

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