ELSEVIER

Carbohydrate Polymers 41 (2000) 277–283

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Preparation of starch betainate: a novel cationic starch derivative

H. Granö[a,*], J. Yli-Kauhaluoma[a], T. Suortti[b], J. Käki[c], K. Nurmi[c]

[a]*VTT Technical Research Centre of Finland, Chemical Technology, P.O. Box 1401, FIN-02044 VTT, Finland*
[b]*VTT Technical Research Centre of Finland, Biotechnology and Food Research, P.O. Box 1500, FIN-02044 VTT, Finland*
[c]*Raisio Chemicals Ltd, P.O. Box 101, FIN-21201 Raisio, Finland*

Accepted 20 September 1999

Abstract

A novel cationic starch derivative was prepared by esterifying native potato starch with anhydrous betaine. The reaction was performed on native potato starch using betainyl chloride in refluxing 1,4-dioxane with pyridine as a nucleophilic catalyst. The product was characterized spectrometrically and its molecular weight distribution was determined. Additionally, the applicability of starch betainate for paper manufacturing was studied. The product is considered to be environmentally more friendly than the traditional cationic starch ethers currently in commercial use as it consists solely of natural and biodegradable products. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Starch betainate; Cationic starches; Paper manufacturing

1. Introduction

Cationic starches are commercially significant starch derivatives used in large quantities as wet-end additives in the paper industry in order to improve retention, drainage and strength (Rutenberg & Solarek, 1984). In 1997, more than 1.5 million tonnes of starch were used for paper manufacturing in Western Europe alone. About 33% of this amount was cationic starches (Bergh, 1998). Cationic starches can be prepared by reaction of starch with reagents containing amino, imino, ammonium, sulfonium or phosphonium groups, all of which can carry a positive charge (Solarek, 1986). However, the present commercially significant types of cationic starches are tertiary aminoalkyl ethers and quaternary ammonium alkyl ethers.

The objective of this work was to prepare a novel cationic starch ester derivative consisting exclusively of natural products, namely starch and betaine, and to examine its applicability for paper manufacture. Starch betainate was prepared by linking betaine (Scheme 1), (carboxymethyl)-trimethylammonium hydroxide inner salt, to starch through an ester bond (Granö, Hase & Yli-Kauhaluoma, 1998). Betaine, like starch, is a natural product which is found in most green plants. It is especially abundant in sugar beets (*Beta vulgaris* var. *altissima* Döll). Linking the cationic substituent to the starch backbone through an ester bond should result in a more biodegradable product than the traditional cationic starch ethers.

2. Experimental

2.1. Materials

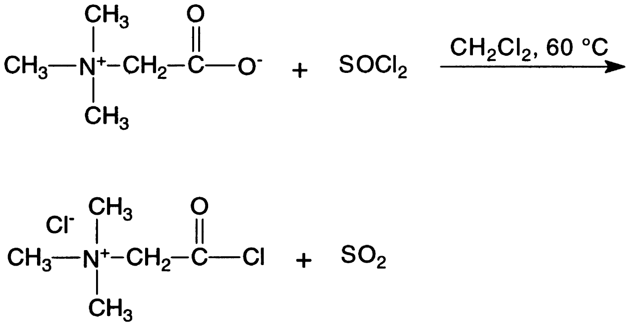
Native potato starch was provided by Raision Tehtaat Oy Ab (Raisio, Finland). It was dried for 3 days at 107°C. Anhydrous betaine internal salt was purchased from Merck (Darmstadt, Germany). 1,4-Dioxane was purchased from Riedel-deHaën (Seelze, Germany) and distilled over sodium-benzophenone ketyl. Diethyl ether was purchased from Rathburn (Walkerburn, UK) and distilled over sodium-benzophenone ketyl. Dichloromethane was purchased from Riedel-deHaën (Seelze, Germany) and distilled over calcium hydride. All the distilled solvents were stored under argon. Pyridine was dried over 4 Å molecular sieves and used without further purification. All other reagents were commercially available and were used as such.

A bleached sulfate pulp consisting of birch and pine (60/40) was used as a raw material for the paper sheets, which were prepared for testing the influence of starch betainate on the mechanical strength properties of paper. Native potato starch was used as a reference in the paper tests. In addition, paper sheets containing no added starch were prepared and tested as references.

---

* Corresponding author.
E-mail address: hanna.grano@vtt.fi (H. Granö)

0144-8617/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0144-8617(99)00146-0



Scheme 1.

2.2. Methods

2.2.1. Characterization of starch betainate

The degrees of substitution (DS) of the prepared starch betainates were determined by Kjeldahl nitrogen analysis on a Tecator Auto 1030-analyzer. Starch betainates and reaction intermediates were analyzed by FTIR spectrometry as KBr-tablets on a Perkin Elmer FTIR Spectrometer 1760X in the 4000–300 cm^{-1} region. Their ^{13}C NMR spectra were recorded at 50°C in deuterium oxide (D_2O) containing 10% (methyl sulfoxide)-d_6 (DMSO-d_6) as standard at 150 MHz with a Varian Unity 600 Spectrometer. The chemical shift 39.7 ppm of DMSO-d_6 was used as a reference in the ^{13}C NMR spectra. Betainyl chloride was not characterized by ^{13}C NMR spectrometry due to solubility problems. All reactions were performed under a positive atmosphere of argon unless otherwise stated.

The size-exclusion chromatographic (SEC) instrument used for determining the molecular weight distributions of the starch betainate samples consisted of an M-616 pump, an M-715 automatic injector, Styragel HT5 (7.8 mm × 300 mm) or Solid Bead A-3 (10 mm × 250 mm) columns at 70°C and an M-410 refractive index detector containing a PDI2000 dual angle laser light scattering detector. Eluent was dimethyl sulfoxide containing 0.5% LiCl at a flow-rate of 0.5 ml min^{-1}. The chromatographic system was controlled by a Millenium 3.05 workstation and the data was handled by a program supplied by laser light scattering detector manufacturer (Precision Detectors Inc., Amherst, MA, USA). All chromatographic hardware was supplied by Waters Corp. (Milford, MA, USA) with exception of the Solid Bead A-3 column, which was supplied by Jordi Assoc. Inc. (Bellingham, MA, USA). All samples were dissolved in chromatographic eluent at 2 g l^{-1} concentration by stirring overnight. The d*n*/d*c* value of 0.066 (Yokoyama, Renner-Nartz & Shoemaker, 1998) reported for starch in DMSO was used for all samples.

2.2.2. Paper tests

The pulp was submitted to wet disintegration according to the standard “SCAN-C 18:65 Disintegration of Chemical Pulp for Testing” (Scandinavian Pulp, Paper and Board Testing Committee, Stockholm, Sweden). The beating of the pulp was performed with a Valley-Hollander apparatus (SCAN-C 19:65 Drainability of Pulp by the Schopper-Riegler Method) and the degree of beating was measured with a Schopper-Riegler number, which was 24 for the birch pulp and 32 for the pine pulp (SCAN-C 19:65). The starches used in the paper tests were thermally gelatinized (25 min at 95–100°C) to give a 0.5% aqueous solution and the gelatinized starches were used within 5 h. The starch solutions were held at ambient temperature before use.

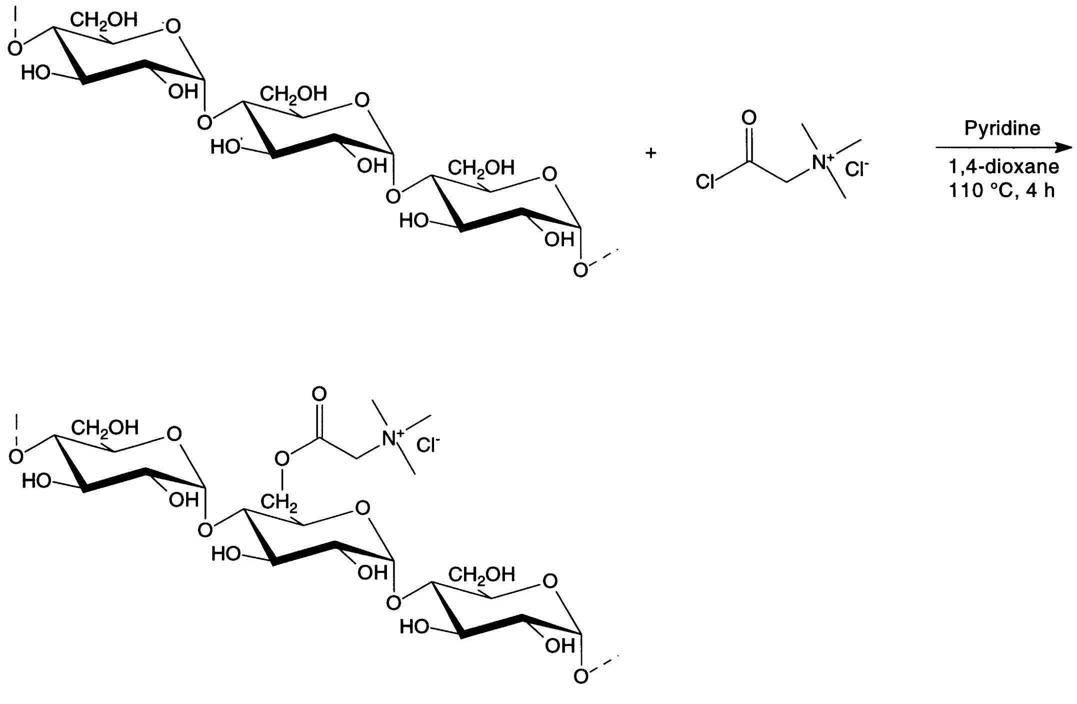
The adsorption experiments of starch onto the pulp fibers were performed at room temperature and the fiber concentration was 1.8% in 1.0 l of water. The starch solution described in the previous paragraph was added to the water–pulp mixture to give a starch concentration of 0.6 or 1.8% based on the weight of pulp fibers. The adsorption time was 5 min. The samples were agitated with a magnetic stirrer. The samples were then poured into a semi-automatic sheet former and diluted to 0.18% concentration. The paper hand sheets were prepared according to the standard “SCAN-C 26:76 Pulp-Preparation of Laboratory Sheets for Physical Testing” using an L&W semi-automatic sheet mould FI 106 (Lorentzen and Wettre, Kista, Sweden), an L&W pneumatic sheet press (Lorentzen and Wettre, Kista, Sweden) and an L&W tumble drier FI 119 (Lorentzen and Wettre, Kista, Sweden). The hand sheets were prepared to a basis weight of 60 g m^{-2}. Water samples for retention estimations were taken from the water coming from the sheet former.

The hand sheets were tested for tensile strength (SCAN-P 38:80 Paper and Board—Tensile Strength, Stretch and Tensile Energy Absorption) and tear resistance (SCAN-P 11:73 Tearing Resistance of Paper and Board) in a conditioned room at a temperature of 23°C and a relative humidity of 50% (SCAN-P 2:75 Paper and Board—Conditioning of Test Samples). The tear resistances were tested with a digital tear resistance Messmer M454 apparatus (Messmer Buchel, Gravesend, UK). The turbidities of the water samples were tested with a HACH 2100AN IS-turbidimeter (HACH Company, Loveland, CO, USA) to afford estimates of the retention.

2.3. Synthesis of betainyl chloride

Betainyl chloride used as an esterification reagent was prepared from anhydrous betaine and thionyl chloride according to an improved version of a synthesis reported by Ito, Hayoshi and Fujino (1973).

Anhydrous betaine (30.0 g, 0.256 mol) was suspended in 45 ml of dry dichloromethane in a three-necked round-bottomed flask. Thionyl chloride (45 ml, 0.617 mol) was added dropwise under constant stirring during a period of 60 min. Sulfur dioxide evolving during the reaction was led through an oil bubbler into an Erlenmeyer flask containing an aqueous KOH solution. The reaction was allowed to proceed at 60°C in an oil bath, until the evolution of gas ceased. Excess thionyl chloride and solvent were then



Scheme 2.

removed by evaporation under reduced pressure. The product was washed four times by suspension in 100 ml of dry diethyl ether with subsequent removal of the solvent by decantation. The crude product was finally suspended in a mixture of 60 ml of diethyl ether and 40 ml of dichloromethane, collected by filtration and dried in vacuo to afford 41.3 g of white powder. The product was stored under argon at 4°C. FTIR (cm^{-1}): 2958 (s, alkyl), 1790 (s, –COCl), 1476 (s, $–CH_2–$), 1460 (w, $–CH_3$).

2.4. Synthesis of starch betainate

Starch betainate was synthesized according to a modification of generally known methods for the esterification of starch with an acid chloride (Lower, 1996).

Native potato starch (15.0 g, 92.5 mmol) was stirred in refluxing pyridine (23.0 ml, 284 mmol, 1 equiv.) for 30 min before 200 ml of dry 1,4-dioxane was added. Solid betainyl chloride (15.9 g, 92.4 mmol, 1/3 equiv., corresponding to a theoretical DS of 1) was slowly added under vigorous stirring. The reaction mixture was heated to 110°C in an oil bath and refluxed gently for 4 h with constant stirring. The reaction mixture was allowed to cool to room temperature before the solvent was decanted. The crude product was dispersed in 200 ml of water. Ethanol (1.5 l) was added to precipitate the starch ester, which was collected by filtration and purified by suspending it repeatedly in 150 ml of ethanol or in a mixture of ethanol and diethyl ether (1:1). The product was finally dried overnight at 60°C to give 14.5 g of starch betainate with a DS of 0.2. IR (cm^{-1}): 3393 (br, –OH), 2926 (s, alkyl), 1756 (s, C=O), 1490 and 1478 (w, alkyl), 1412 (w, > NMe), 1256 and 1201 (w, $–CO_2–$), 1152 (m, –C–O–C–), 1024 (m, –OH). ^{13}C NMR (150 MHz, DMSO-d_6) δ 55.9 ($–CH_3$), 65.1 ($–CH_2–$), 166.5 and 166.0 (C=O), 101.4 (C-1), 74.9 (C-2), 72.9 (C-3), 79.1 (C-4), 73.2 (C-5), 62.2 (C-6).

3. Results and discussion

We were attracted to embark on the preparation of starch betainate by two reasons. Starch betainate consists of two abundant natural products, starch and betaine, and it can thus be considered environmentally more friendly than current cationic starches in commercial use. We also found it interesting to study the characteristics of starch betainate in papermaking processes.

3.1. Synthesis of betainyl chloride

The esterification reagent, betainyl chloride, was prepared from anhydrous betaine by treating it with thionyl chloride in dichloromethane at 60°C (Scheme 1). The crude product contained unidentified colored by-products, which caused problems in initial work. However, it was found that extractions with diethyl ether removed the colored by-products, but by IR analyses, the slightly purified product proved to be a mixture of the desired acid chloride and of betaine hydrochloride. Attempts were also made to prepare betainyl chloride from anhydrous betaine and other chlorinating agents such as oxalyl chloride and phosphorus pentachloride. The acid chlorides from these reactions lacked the colored impurities, but the equilibrium between

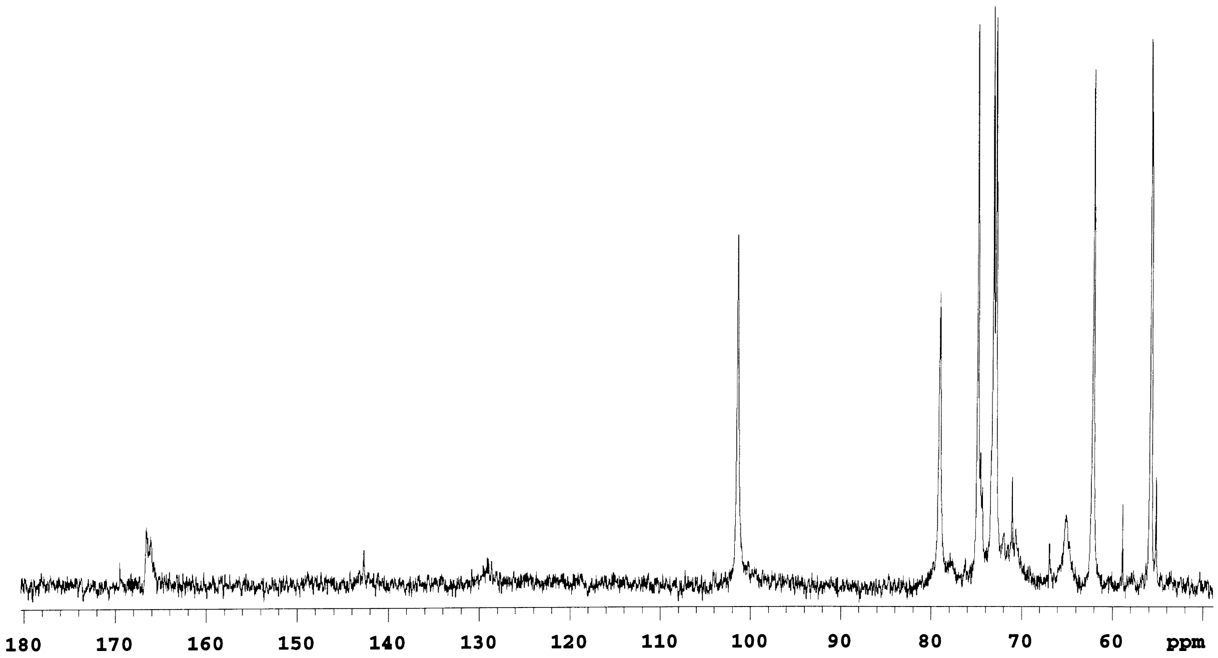


Fig. 1. The ^{13}C NMR of starch betainate in D_2O containing 10% DMSO-d_6.

acid chloride and betaine hydrochloride in the product mixture was shifted unfavorably towards betaine hydrochloride in comparison to the product obtained from the reaction with thionyl chloride. It was not possible to determine the exact yield of any of these reactions, since the components of the product mixture could not be separated. In theory, betaine hydrochloride should react with a chlorinating agent to yield betainyl chloride as well. Presumably, this reaction did not take place due to the poor solubility of betaine hydrochloride in dichloromethane.

For environmental as well as economical reasons, it would have been interesting to perform the esterification reactions in water slurry systems. As a carboxylic acid chloride is too reactive for such esterification reactions, several attempts were made to synthesize a betaine anhydride from betaine hydrochloride. Several general reagents and methods for the preparation of carboxylic acid anhydrides were investigated, including acetic anhydride, oxalyl chloride in combination with *N*,*N*-dimethylformamide, thionyl chloride in combination with pyridine, and *N*,*N*′-dicyclohexylcarbodiimide (DCC). These methods did not afford the desired acid anhydride.

3.2. Synthesis of starch betainate

The esterification of starch with betainyl chloride was performed according to previously known methods (Scheme 2). Several authors have reported the use of pyridine as a nucleophilic catalyst for esterification reactions (Degering, 1954; Whistler, 1945). Various common organic solvents have been used in starch esterifications. Roberts (1967) reported the use of benzene or toluene for this purpose. In a recent patent, Peltonen and Harju (1996) reported the use of *N*,*N*-dialkylformamides as solvents for esterification of starch with fatty acid chlorides. Additionally, starch has been esterified with carboxylic acid chlorides in 1,4-dioxane (Teng & Rha, 1972) and carbon tetrachloride (Zhao, Madson & Whistler, 1996). A comprehensive review article on the preparation of acid esters of starch has been published by Lower (1996).

In this work, native potato starch was stirred in refluxing pyridine prior to the esterification reaction in order to swell the starch granules and to facilitate contact between starch hydroxyl groups and betainyl chloride. The suitability of different solvents and catalysts for the esterification reaction was then examined. 1,4-Dioxane proved to be the best solvent. The esterification did proceed in toluene as well, but yields were lower. No esterification was found to take place in *N*,*N*-dimethylformamide or dichloromethane. The use of triethylamine instead of pyridine as a nucleophilic catalyst was studied as well, but this reaction resulted in black crystalline products of unidentified nature. The best yields were obtained in refluxing 1,4-dioxane using pyridine as a nucleophilic catalyst in the presence of starch and betainyl chloride. However, the esterification reactions did not proceed to completion and no products with degrees of substitution exceeding 1 were prepared during this work. The crude reaction products were purified by precipitating them from water by adding ethanol to the mixture and by solvent extractions with ethanol and diethyl ether.

3.3. Characterization of starch betainate

The degrees of substitution of the prepared starch

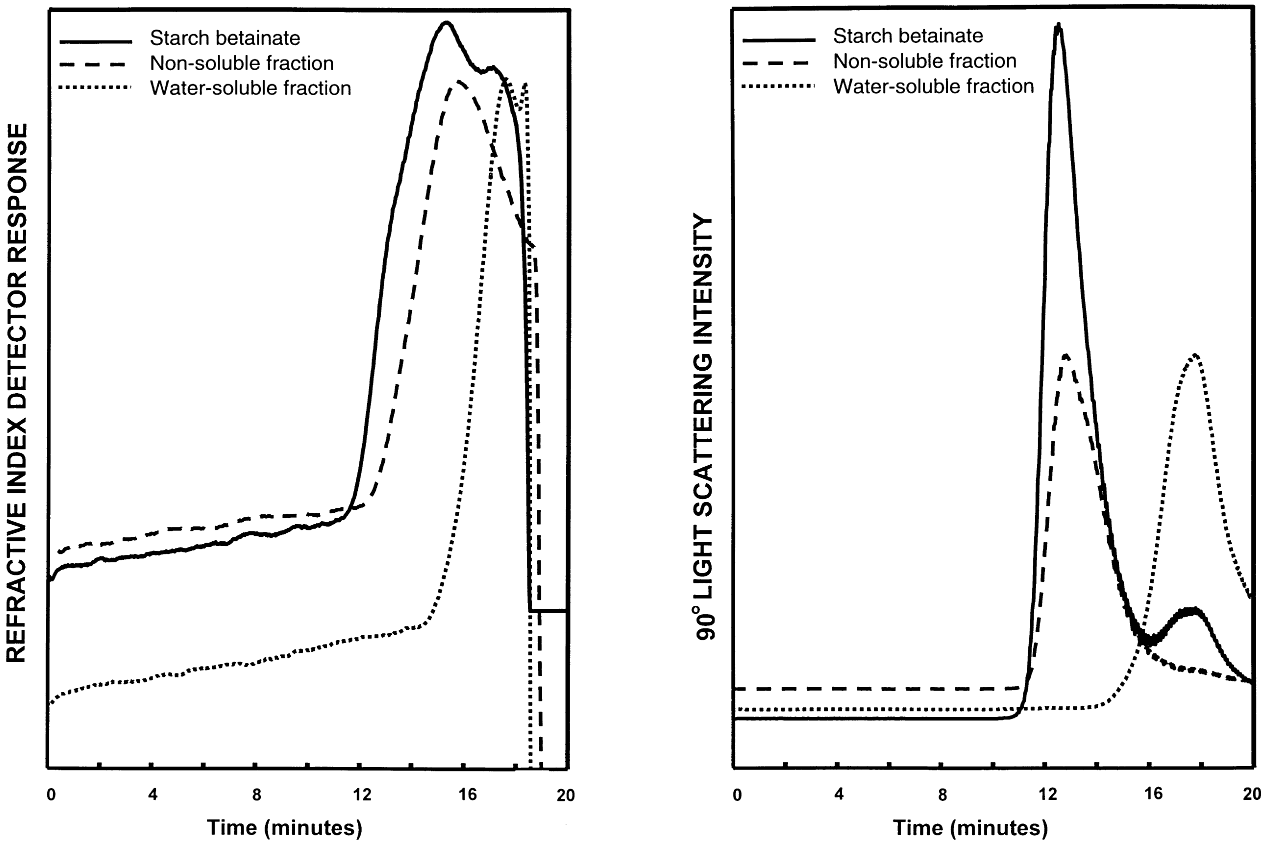


Fig. 2. Chromatograms of original starch betainate and its water-soluble and non-soluble fractions on Styragel HT5 column. Detection by refractive index detection (on left) and right-angle laser scattering (on right).

betainates varied from 0.01 to 1 depending on the amount of added betainyl chloride. Products of higher DS were not prepared. The products of higher DS were discolored. The origin of the color remains unknown.

The prepared starch betainates were characterized by ^{13}C NMR and IR spectrometry. In the IR spectra of the starch betainates, an absorption band assigned to the carbonyl stretching of the ester bond could be detected at 1756 cm^{-1}. This differed markedly from the carbonyl stretching absorption bands of 1790, 1730 and 1636 cm^{-1} observed for betainyl chloride, betaine hydrochloride and anhydrous betaine, respectively. In the ^{13}C NMR spectra of the starch betainates, a split carbonyl peak assigned to the ester carbonyl group could be observed at δ 166 ppm (Fig. 1). Further, chemical shifts assigned to the betainyl substituents could clearly be detected in the ^{13}C NMR spectra. The starch betainate *N*-methyl signals were found at δ 55.9 ppm and the *N*-methylene signal at δ 65.1 ppm. These chemical shifts correspond well to the reference shifts measured for anhydrous betaine, namely δ 55.0 and 68.0 ppm. The chemical shift assigned to the inner salt carboxyl carbon of anhydrous betaine could be found at δ 170 ppm in the reference spectrum. Although some splitting of the starch carbon signals could be observed in the ^{13}C NMR spectra, it was not possible to determine which starch hydroxyl was the preferred target for esterification. As the ester carbonyl peak was split into two peaks of approximately equal intensity, it seems that the primary hydroxyl group was not substantially preferred over the secondary ones.

The starch betainates of higher DS were soluble in water. However, on dissolving the starch betainates in water at room temperature, part of the samples remained undissolved. This result implied that the starches were not homogeneously esterified. Further analyses did indeed indicate that the non-water-soluble fractions consisted of unmodified starch whereas the water-soluble fractions were esterified. Analysis of the molecular weight distribution of the soluble and the non-water-soluble fractions demonstrated that both fractions had molecular weights over 1 000 000, although the soluble, esterified fraction had a slightly lower molecular weight distribution in comparison to the non-water-soluble fraction (Fig. 2). Both chromatographic systems utilized for these analyses were capable of separating the water-soluble and non-water-soluble fractions. In both systems, the water-soluble esterified fraction could be distinguished as a shoulder peak in the original synthesis product sample (Fig. 2). First the results from laser light scattering detector revealed that the separation of the water-soluble and non-water-soluble fractions was due to non-SEC chromatographic effect as the weight average molecular-weights (M_w) of both fractions were rather similar, about

Table 1
The effect of different starch types on the retention and the mechanical properties of paper

Entry	Starch type	DS	Tear index (mN m^2 g^{-1})	Tensile index (N m g^{-1})	Turbidity (NTU)
1	No added starch	–	10.7	44	3.3
2	Native starch, 0.6%	–	12.3	60	1.7
3	Native starch, 1.8%	–	12.5	67	1.9
4	Starch betainate, 0.6%	0.44	12.7	65	Not available
5	Starch betainate, 1.8%	0.44	13.2	59	2.0

1 000 000 (for both fractions same refractive index was used as no refractive index for starch betainate was available, but this could lead to not more than 20% error).

3.4. Paper tests

The suitability of starch betainate as a wet-end additive in paper manufacturing was studied. Paper sheets containing starch betainate were prepared and tested, and the results were compared to the corresponding results obtained from the tests of paper sheets containing no starch and native potato starch (Table 1). Prepared paper sheets were tested for tensile strength and tear resistance. In addition, the effect of added starch on retention was evaluated by measuring the turbidity of the water coming from the sheet former during the preparation of the paper sheets. Turbidity is reported as NTU (nephelometric turbidity unit). Retention properties are known to improve with decreasing NTU values.

The paper tests showed that starch betainate possesses new and promising features as an environmentally friendly cationic paper additive. The paper tests demonstrated that starch betainate increases paper strength considerably. The tensile index and thus the tensile strength of the paper sheets containing 0.6% of a starch betainate with a DS of 0.44 increased markedly compared to the paper sheets containing 0.6% of native starch or the paper sheets containing no starch at all (Table 1, entries 1, 2 and 4). However, paper sheets containing 1.8% of native starch had a higher tensile strength than paper sheets containing 1.8% of starch betainate (Table 1, entries 3 and 5). Thus, it seems that addition of small amounts of starch betainate to the pulp influences the tensile strength beneficially, but this effect seems to decrease when the amounts of added starch betainate are increased. Nevertheless, the tensile strength of paper sheets containing 1.8% of starch betainate is still substantially higher than the tensile strength of paper sheets without added starch. The tear resistances of paper sheets containing starch betainate seem to be superior to the corresponding tear resistances of paper sheets containing native potato starch for all concentrations of added starch (Table 1, entries 2–5). Indeed, the tear resistances for the starch betainate paper sheets seem to improve more sharply with increasing concentrations in the paper than do the tear resistances for paper sheets containing native potato starch (Table 1, entries 2–5). The retention properties of starch betainate seem to be in line with those of native potato starch.

4. Conclusions

A new cationic starch ester was prepared by reacting starch with betainyl chloride in refluxing 1,4-dioxane in the presence of pyridine as a nucleophilic catalyst. Starch betainate was characterized by IR and ^{13}C NMR spectrometry and its suitability as a wet-end additive in paper manufacturing was studied. Starch betainate was found to increase the strength of paper sheets and to have beneficial influence on retention. We are currently further studying the influence of different degrees of substitution as well as different concentrations of the added starch betainate on paper sheet characteristics and preparing several types of new starch ester derivatives of naturally occurring nitrogen containing compounds.

Acknowledgements

This work was supported by TEKES (Technology Development Centre, Helsinki, Finland). We are grateful to Juha Saari (VTT) for performing the paper tests and to Professor Anneli Hase (VTT) for helpful discussions.

References

Bergh, N.-O. (1998). Die Bedeutung der Stärke bei der Papierherstellung. 1. PTS-Symposium 1998: Einsatz von Stärke bei der Papiererzeugung, Papiertechnische Stiftung, Munich.

Degering, E. F. (1954). In J. A. Radley (Ed.), 3. (pp. 298–331). *Starch and its derivatives*, 1. New York: Wiley.

Granö, H., Hase, A., & Yli-Kauhaluoma, J. T. (1998). Uusi kationinen tärkkelys, sen valmistus ja käyttö. Finnish Patent Application FI 981991.

Ito, S., Hayoshi, T., & Fujino, Y. (1973). Reductive preparation of choline from betaine. *Research Bulletin of Obihiro University*, *8*, 99–103.

Lower, E. S. (1996). Starch, fatty, organic and inorganic acid esters. *Riv. Ital. Sostanze Grasse*, *73*, 159–163.

Peltonen, S., & Harju, K. (1996). Applications and methods for the preparation of fatty acid esters of polysaccharides. US Patent, 5 (1996) 589 577.

Roberts, H. J. (1967). Starch derivatives. In R. L. Whistler & E. F. Paschall (Eds.), (pp. 297–312). *Starch: chemistry and technology*, II. New York: Academic Press.

Rutenberg, M. W., & Solarek, D. (1984). Starch derivatives: production and uses. In R. L. Whistler & J. N. BeMiller & E. F. Paschall (Eds.), *Starch: chemistry and technology*, 2. (pp. 354–364). San Diego, CA: Academic Press.

Solarek, D. B. (1986). Cationic starches. In O. D. Wurzburg (Ed.), *Modified starches: properties and uses*, (pp. 113–129). Boca Raton, FL: CRC Press.

Teng, J., & Rha, C. (1972). Chewing gum. US Patent, 3 666, 492.

Whistler, R. L. (1945). Preparation and properties of starch esters. *Advances in Carbohydrate Chemistry*, *1*, 279–307.

Yokoyama, W., Renner-Nartz, J. J., & Shoemaker, C. F. (1998). Starch molecular mass and size by size exclusion chromatography in DMSO–LiBr coupled with multiple angle laser light scattering. *Cereal Chemistry*, *75*, 530–535.

Zhao, J., Madson, M. A., & Whistler, R. L. (1996). Cavities in porous corn starch provide a larger storage space. *Cereal Chemistry*, *73*, 379–380.