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1 **Impact of the coating process on the molecular structure of starch-based barrier**

2 **coatings**

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7

8 **ABSTRACT**

9 Molecular analysis of starch structure can be used to explain and predict changes in physical properties,

10 such as water vapor and oxygen barrier properties in packaging materials. Solution casting is a widely

11 used technique to create films from starch formulations. This study compared the molecular properties

12 of these standard films with those of experimental coatings applied to paper in laboratory-scale and

13 pilot-scale trials, with all three techniques using the same starch formulation. The results revealed large

14 differences in molecular structure, i.e., cross-linking and hydrolysis, between films and coatings. The

15 main differences were due to the shorter drying time allowed to laboratory-scale coatings and the

16 accelerated drying process in pilot trials owing to the high energy output of infrared dryers. Furthermore,

17 surface morphology was highly affected by the coating technique used, with a rougher surface and

18 many pinholes occurring in pilot-scale coatings, giving lower water vapor permeability than laboratory-

19 scale coatings.

20 **KEYWORDS** starch, film forming, coating, solution cast, molecular structure, citric acid, drying,

21 processing

22

INTRODUCTION

24 There is increasing demand for green packaging materials in the world, driven by industrial growth and

25 trends for environmentally friendly packaging.[1] The world demand for food packaging is expected to

26 grow about 2.5% per year.[2] The expected production capacity of bio-plastics is ecpected to grow fivefold

27 from 2011 to 2016 as the largest sector in packaging.[3] Hence, there have been intensive investigations

28 on bio-based materials, especially from bio-polymers, for packaging purposes. Conventional food

29 packaging consists of multi-layer films of synthetic plastics and adhesives to provide barrier properties,

30 allow color printing, and bind all layers together. From an environmental point of view, it is desirable to

31 replace these coatings with renewable types. Several bio-polymers such as starch, poly-lactic acid, and

32 polyhydroxybutyrate can replace synthetic plastics such as polyethylene terephthalate or polystyrene

33 plastics.[4,5] In 2010, starch represented the second largest sector of the global bio-plastic packaging

34 market, accounting for 22.2%.[6] Starch is a widely used bio-polymer for the production of films and

35 coatings because of its abundance and ability to form a network structure. The possibility of using starch
36 as a base in new materials has been extensively researched since the 1950s.[7] Starch is commonly
37 plasticized with glycerol to overcome its brittleness and several chemical modifications can be used to
38 improve the hydrophilic character of starch. Due to its structure of chains of (1→4) linked α-glucan units
39 and numerous free hydroxyl groups, various chemical modifications such as acid hydrolysis, oxidation,[8]
40 cross-linking,[9] and acetylation[10,11] can be applied to obtain desired physical properties. Regarding barrier
41 properties for food packaging, the most critical compounds are water vapor and oxygen, since these
42 compounds can permeate through the packaging material and alter the food quality. In recent studies,
43 cross-linking with citric acid (CA) has been cited as a promising additive to improve the thermal and
44 barrier properties of starch films.[9,12,13] In those studies, changes in molecular structure due to acid
45 hydrolysis and cross-linking by adding CA were analyzed using solution-cast films.[12] In a study by Olsson
46 et al.,[9] starch films containing up to 30pph CA reduced moisture content, diffusion coefficient and water
47 vapor permeability confirming previous findings.[13,14] Molecular characterization studies on the same
48 films confirmed that high CA content and high temperature curing increased cross-linking reactions, but
49 that hydrolysis of starch occurred simultaneously. To prevent severe hydrolysis of starch films at high CA
50 content and preserve improved barrier properties at the same time, pH adjustments to the starch
51 formulation before drying were tested. It was shown that at pH 4, starch hydrolysis was stopped, while
52 cross-linking still occurred. In addition, gas barrier properties, i.e., oxygen and water vapor permeability,
53 showed a minimum at pH 4 measured on laboratory-scale coated paper based on the same starch
54 solution and prepared under comparable drying conditions.[9,15] However, to the best of our knowledge,
55 there are no studies comparing the impact of the coating process on the molecular structure of starch
56 coated on paper or paperboard, either in the laboratory or at pilot scale, relative to solution-cast films.

57 To test a new starch formulation as a barrier coating in a food packaging application, pilot-scale trials are
58 normally carried out in industry. However, such trials are very expensive and time-consuming. As an
59 alternative, laboratory-scale experiments can be used to study desired parameters. The most common
60 film formation technique used at laboratory scale is casting, where the film-forming solution is cast on a
61 non-adhesive surface and the solvent is evaporated. Different parameters such as drying temperature
62 and relative humidity (RH) influence the film properties. For instance, it has been shown that in glycerol-
63 plasticized amylopectin films, increasing RH results in higher relative crystallinity during film formation.[16]
64 Throughout the drying process, hydrogen bonds are formed between the bio-polymers and/or
65 plasticizers and the film structure is generated.[17] The longer film formation takes, the longer time there
66 is for a film component to phase-separate and crystallize.[18] However, drying kinetics in industry can
67 differ substantially from laboratory-scale conditions. For example, in industrial applications the drying
68 strategy depends on the machine speed, amount of layers applied and the drying conditions, i.e.,
69 temperature and relative humidity in the building. There is only a short time between the application of
70 the coating on the carrier material and the final immobilization point where water evaporates and the
71 network structure is created. Therefore, it is crucial to study and understand the relationship between
72 processing technique, molecular structure, and material properties when seeking to develop new
73 functional packaging coatings.

74   The objectives of this study were terefore: 1) to find suitable methods to analyze the molecular
75   structure of starch in paper coatings, 2) to determine the impact of the coating process parameters on
76   the molecular and barrier properties of starch-based coatings, and 3) to compare the molecular
77   structure of solution-cast starch films and laboratory-scale coated papers with that of industrially
78   produced starch coatings from a pilot trial. Experimental parameters for the pilot trial were chosen
79   according to a previous study,[15] where laboratory-scale coated papers showed a minimum in water
80   vapor transmission rate (WVTR) and no hydrolysis when the pH was kept at 4 for a CA-starch
81   formulation. That study showed that molecular changes in solution-cast films cannot be directly related
82   to barrier properties that are generally measured on coated papers. There were large differences in
83   molecular structure between solution-cast films and laboratory-scale coated papers. No hydrolysis was
84   detectable due to the shorter drying time applied to the laboratory-scale coatings. The pilot-scale
85   coatings also showed no hydrolysis, but demonstrated a higher degree of cross-linking compared with
86   the laboratory-scale coated papers and solution-cast films. At pilot scale, the drying process is
87   accelerated by the high energy output of infrared dryers, which evaporates the water in a very short
88   time and initiates the esterification and finally cross-linking reaction. The higher water vapor
89   permeability in pilot-scale coatings has been attributed to a rougher and more uneven surface and large
90   visible pinholes compared with laboratory-scale coatings due to the coating technique applied.

91

92   **EXPERIMENTAL**

93   **Materials**

94   Hydroxypropylated and oxidized potato starch (Solcoat 155 and Solcoat P55) was kindly provided by
95   Solam (Kristianstad, Sweden). According to the supplier, this commercial starch contains about 79%
96   amylopectin and 21% amylose, with a degree of substitution of 0.11 with respect to hydroxypropylation.
97   A different starch was used in the pilot trial because of the lower viscosity requirements in industrial
98   applications and the higher solids content while boiling (30% for Solcoat P55 instead of 20% as for
99   Solcoat 155). The starch used in laboratory coatings had a viscosity of 180 cP at 20% solids content,
100   Brookfield LVDV 100 rpm, and 50 °C, for jet cooked starch whereas the pilot-scale starch had a viscosity
101   of 30 cP under similar conditions. The difference between the two starches (Figures 1 and 2) is due to
102   higher oxidation in Solcoat P55 to gain lower viscosity set by the amount of hypochlorite during
103   modification. All reagents and solvents (sodium hydroxide, phenol, sulfuric acid 95-97%, double
104   supplemented iodine, anhydrous glucose, potassium hydroxide, boric acid, copper(II)sulfate-5 hydrate)
105   used for analyses were of analytical grade and were purchased from Merck, Germany, except for
106   anhydrous citric acid and sodium borate-10hydrate, which were supplied by Sigma-Aldrich Inc., ST. Louis,
107   MO, USA.

108   **Preparation of starch films and starch coatings**

109   ***Solution-cast starch films***

110   The preparation of solution-cast starch films is described in detail elsewhere.[9] In brief, a 10% (w/w)
111   starch (Solcoat 155) solution was gelatinized in a boiling water bath, cooled to room temperature and 30
112   parts CA per 100 parts of dry starch (pph) were added. The CA-containing starch solution was then
113   adjusted to different pH values (2, 4 and 6.5) using 10 M NaOH solution, cast in Petri dishes and dried at
114   70 °C for 5 h. The dried solution-cast films were heat-treated (cured) for 10 min at 150 °C.

115   *Laboratory-scale starch coatings on paper*

116   The laboratory-scale starch coatings were prepared according to Olsson et al.[15] The pH-adjusted starch
117   (Solcoat 155) solutions described above were coated in double layers on Super Perga WS Parchment
118   70 g/m^2 paper (Nordic Paper Greåker, Norway) using a bench coater and a wire-wound bar (K202
119   Control Coater, RK Coat Instrument Ltd., Royston, UK). The first layer was dried before applying the
120   second layer and both coated layers were dried at either 70 °C or 150 °C for 90 s. The coat weight was
121   measured according to Olsson et al.[15] In brief, the difference in weight between coated and uncoated
122   papers was measured after conditioning at 23 °C and 50% RH for at least 24 h. The resulting coat weight
123   was between 15 and 18 g/m^2.

124   *Pilot-scale starch coatings on paper*

125   Pilot-scale coating was carried out using an industrial machine (UMV Coating Systems AB, Säffle, Sweden)
126   and a starch (Solcoat P55) formulation with pH adjusted to 4. The coatings were applied either as single
127   or double layers. The machine parameters were: machine speed 400 m/min, coating technique hard tip,
128   drying with infrared dryer at 150 °C, followed by 60 °C at 35% RH, and a nominal evaporation rate of 673
129   kg/m/h. The starch formulation consisted of 100 pph starch and 30 pph CA, adjusted to pH 4 with NaOH
130   and 0.01% (w/w) defoamer BIM 7640 (BIM Kemi Sweden AB).. Two commonly used and well-studied
131   industrial clay fillers, 87pph kaolin filler (Barrisurf LX^{TM}, Imerys) and 3pph nanosized clay filler (Cloisite
132   Na$^+$ TM, Southern Clay Products Inc.), were added to improve barrier properties and develop a
133   renewable starch formulation for industrial usage. The resulting coat weight was 6 and 11 g/m^2 for
134   single and double coatings, respectively, on greaseproof paper Super Perga WS Parchment 70 g/m^2
135   (Nordic Paper Greåker, Norway).

136   **Extraction of starch from the coated paper**

137   A method to extract starch from the coated carrier material (paper) was developed in order to ensure a
138   representative comparison of the molecular structure in solution-cast films and coated papers. Cut
139   pieces of coated paper (0.5 x 0.5 cm, 0.1 g) were either stirred in water or in 0.1 M or 1 M NaOH for
140   different periods (20 min, 5 h, 24 h). The extract was filtered through 0.45 µm filters. Starch content in
141   terms of glucose concentration was measured according to the phenol-sulfuric acid method.[19] The
142   uncoated carrier material used as a blank was treated in a similar way.

143   **Molecular characterization of amylose and amylopectin**

144 Changes in amylose and amylopectin content were determined using a method described elsewhere.[12]
145 In brief, 25 mg solution-cast film or 100 mg starch-coated paper were dispersed in 5 mL 0.1 M NaOH,
146 filtered through an 0.45 μm filter, and a 1-mL aliquot was injected for size-exclusion chromatography on
147 a Sepharose CL-2B column (GE Healthcare, Uppsala, Sweden). Fractions of 1 mL were analyzed using a
148 combination of the phenol-sulfuric acid method and iodine staining.[19,20] This permitted determination of
149 the starch concentration in the elution profile in terms of glucose equivalents using the phenol-sulfuric
150 acid reagent and determination of chain length in terms of wavelength at maximum absorbance using
151 iodine staining. Amylose molecules appear at higher wavelength numbers due to their longer chains.[20,21]
152 The experiment was performed in duplicate.

Determination of weight-average molecular weight (M_W)

154 Weight-average molecular weight (M_W) was measured on solution-cast starch films and on extracted
155 starch from coatings, which were then dissolved in either 0.1 M NaOH solution or distilled water.
156 Therefore, about 25 mg solution-cast films or 100 mg starch-coated paper were suspended in 5 mL of
157 the respective solvent for 2 h and gently stirred using a magnetic stirrer. The NaOH suspensions were
158 kept at room temperature, while the water suspensions were heated to 70 °C in a water bath to dissolve
159 the starch. The solutions were filtered through a 0.45 μm filter and directly injected (75 μL) into a high-
160 performance size-exclusion chromatography (HPSEC) system coupled with a multi-angle laser-light
161 scattering (MALLS) detector and a refractive index (RI) detector, as described elsewhere.[12] Furthermore,
162 a 950-μL aliquot of the filtered water suspension was treated with 50 μL 2 M NaOH to detect possible
163 changes in M_W due to expected cross-linkage formation between CA and starch. The experiments were
164 performed in duplicate.

Solubility in water

166 Water solubility was determined as described elsewhere.[12] In brief, the starch/water suspensions (about
167 5 mg/mL) was stirred for 2 days and then diluted (1:80, v/v) and filtered before analyzing the starch
168 concentration using the phenol-sulfuric acid reagent.[19] The corresponding glucose concentration was
169 calculated using a glucose standard calibration curve. The glucose concentration was corrected by a
170 factor of 0.9, based on anhydroglucose units (M_{AGU} 162 g/mol) as the main subunits of starch. The
171 experiment was performed in duplicate.

Titration with copper (II)-sulfate for CA di-ester determination

173 Citric acid di-esters were determined according to the complexometric titration method of CA with
174 copper(II)-ions described by Graffmann et al., [22,23] with small modifications as described elsewhere.[12] In
175 brief, 300 mg solution-cast starch film or 1 g starch-coated paper was weighed into a beaker and two
176 different treatments, direct titration and titration after hydrolysis, were carried out. Starch ester bonds
177 were hydrolyzed using 50 mL 0.1 M KOH (pH >12). In both treatments, a borax/boric acid buffer (pH 8.5)
178 was added and the starch samples were titrated with 0.02 M copper(II)-sulfate solution. The content of
179 CA di-ester was calculated according to Menzel et al.[12] The experiment was performed in triplicate.

Scanning electron microscopy of laboratory-scale and pilot-scale coated papers

Scanning electron microscopy was carried out directly on film surfaces using an environmental tabletop Hitachi TM-1000-mu-DeX instrument and an accelerating voltage of 15 keV, magnification x100.

Water vapor transmission rate of pilot-scale coatings compared with laboratory-scale coatings

Barrier properties in terms of WVTR were measured on laboratory-scale and pilot-scale coatings using ISO 2528 with silica gel as desiccant in tests carried out at 23 °C and 50% RH. The experiment was performed in duplicate.

RESULTS AND DISCUSSION

Extraction of starch from the coated papers

Pre-experiments were performed with the laboratory-scale and pilot-scale coated papers to ensure that the entire starch coating went into solution and that particles from the carrier material did not interfere with the analysis. It was found that 100 mg coated material in 5 mL 0.1 M NaOH, stirred for 20 min and subsequently filtered through a 0.45 μm filter, was sufficient to recover 75-82% of the starch applied as a coating. The dissolved starch content was determined as glucose equivalents using phenol-sulfuric acid reagent and a glucose calibration curve. Longer time (5 h, 24 h) or higher alkali concentration (1 M NaOH) did not increase solubility (data not shown). For the pilot-scale coatings, it was found that about 3% (by weight) of the uncoated carrier paper went into the 0.1 M NaOH solution and was recovered as glucose equivalents using phenol-sulfuric acid reagent. However, iodine staining showed no color formation and M_W determined by HPSEC-MALLS-RI was lower than 40,000 g/mol, indicating that the dissolved molecules were probably low molecular weight starch molecules present within the carrier paper. In addition, the elution profile using size-exclusion chromatography of the dissolved part of the uncoated carrier material showed small molecules with no iodine staining eluting late in the chromatogram (Figure 1, elution fraction 135-160 mL). Therefore, these small molecules were considered not to interfere with further molecular analysis.

Molecular changes in laboratory scale starch coatings compared with solution-cast starch films

Molecular characterization

The solution-cast starch films are described in detail by Olsson et al.[15] and were used as reference material for laboratory-scale starch coatings.

Molecular characterization of laboratory-scale coated starch films and solution-cast starch films revealed no changes in amylopectin and amylose distribution (relative absorbance curve and $Λ_{max}$ values) between the laboratory-scale coated starch films at pH 2 at different curing temperatures (non-cured

214   and cured at 150 °C). However, with high temperature curing (150 °C) of the solution-cast starch films,
215   the first eluting peak corresponding to amylopectin was strongly affected at different pH levels due to
216   starch degradation (Figure 2b). For the laboratory-scale coated starch films no degradation of starch
217   molecules was detected and hence no hydrolysis due to CA had taken place compared with the as-
218   received starch (Figure 2a). One explanation could be differences in the drying process of the coatings
219   and films, as the curing time to produce laboratory-scale coated starch papers was substantially shorter
220   (90 s) than that for solution-cast films (10 min). In addition, it is reasonable to believe that heating the
221   coated papers to the same temperature as the solution-cast films took a longer time due to the
222   thickness of the material. It has been shown previously that high temperature promotes acid
223   hydrolysis[12,24,25] and that different drying conditions influence film formation and molecular structure in
224   starch films.[16,26] Hence, during the shorter drying time for the starch coatings, less starch was degraded
225   compared with in the solution-cast films. It is important to consider the drying method applied to
226   coatings and cast films in order to predict molecular changes in solution-cast films coated on paper in
227   the laboratory, as well as coatings prepared under industrial conditions.

228

229   ### M_W determination in 0.1 M NaOH and water

230   Starch from solution-cast films and laboratory-scale coated films were dissolved in 0.1 M NaOH to
231   determine M_W of the de-esterified starch molecules (Figure 3). Solution-cast films as described
232   previously by Olsson et al.[15] were used as reference. The M_W of starch from coatings was between 6.3
233   and 8.0*10^6 g/mol for non-cured and 150 °C cured coatings, compared with 8.8*10^6 g/mol for as-
234   received starch. There were no significant differences (t-test, $p > 0.05$) between coatings prepared in the
235   different conditions, i.e. neither pH nor high temperature curing affected M_W of the starch applied as a
236   coating on paper. This is in agreement with the results from molecular analysis of amylose and
237   amylopectin showing no degradation of starch in laboratory-scale coated paper (Figure 2a). However,
238   solution-cast starch films were strongly affected by pH and high temperature curing e.g., a decrease in
239   M_W with decreasing pH (Figure 3). Adjustment of the pH to higher values prevented acid hydrolysis even
240   in cured films, as shown in a previous study.[15]

241   In addition, the M_W of the water soluble starch extract of solution cast films and laboratory scale
242   coatings was measured before and after subsequent de-esterification with NaOH (Table 1) and the
243   solubility in water was determined (Figure 4).

244   Laboratory-scale coating on paper showed higher water solubility (63-80%) than the reference solution-
245   cast starch films (16-48%, data from Olsson et al.). This could be due to a lower degree of cross-linking of
246   starch molecules by CA in the laboratory-scale starch coatings compared with the solution-cast starch
247   films, resulting in higher water solubility.

248   The M_W of the water-soluble starch extracted from laboratory-scale coated papers was lowest for
249   coatings prepared at pH 2 (5.5*10^6 g/mol) and increased with increasing pH (Table 1). There was no
250   significant change in M_W when coatings were cured at high temperature (150 °C). The M_W of water-

251   soluble starch was similar to that of de-esterified starch in NaOH (Figure 3), as anticipated from the high
252   water solubility. Only coatings prepared at pH 2 had a slightly lower M_W in water (Table 1), although
253   water alone also gave the highest water solubility.

254   Cross-linking of starch by CA was detectable as a change in M_W of the water-soluble starch after
255   subsequent treatment with NaOH which induced hydrolysis of the ester bonds between one CA
256   molecule and two starch molecules and hence reduced M_W(Table 1). The laboratory-scale coated
257   papers prepared at pH 2 showed the highest M_W decrease (23%, or 26% for curing at 150 °C) after NaOH
258   treatment of the water-soluble starch. The M_W decrease was lower for laboratory-scale coatings
259   prepared at pH 4 (6% non-cured, 16% cured) and pH 6.5 (6% non-cured, 12% cured), indicating fewer CA
260   cross-linkages in the water soluble starch extract. The cross-linking reaction, which is basically Fischer
261   esterification, is catalyzed at low pH explaining the larger decrease in M_W at pH 2. High-temperature
262   curing of the coatings resulted in slightly higher M_W decreases after NaOH treatment and hence a higher
263   degree of cross-linking. In contrast, M_W before and after de-esterification of water-soluble starch from
264   solution-cast films was highly affected by both pH-adjustment and curing, resulting in highly cross-linked
265   films at pH 2 (M_W decrease 19%) and high temperature (M_W decrease 85%), as described and discussed
266   in previous reports.[15]

267   It was found that the M_W and solubility of starch from solution-cast films and laboratory-scale coatings
268   were differently affected. The difference in cross-linking might be due to the difference in the drying
269   process, i.e. curing for 10 min or 90 s, as discussed above with reference to the molecular distribution of
270   amylose and amylopectin. However, even the short drying time that was applied to the coated papers
271   was sufficient to initiate cross-linking between starch molecules in laboratory-scale coatings at all pH
272   levels. In addition, the M_W data showed that cross-linking of starch by CA took place, besides acid
273   hydrolysis as described previously.[12,15]

Citric acid di-ester determination in solution-cast starch films and laboratory-scale coated papers

275   As described in previous reports,[12] the titration of CA with copper (II) -sulfate can detect CA and mono-
276   esterified CA molecules. Hence, titration before and after hydrolysis shows the amount of CA molecules
277   that are di-esterified and potentially cross-linked between different starch molecules. The CA di-ester
278   content was expressed in terms of degree of di-esterification (DDE) for the solution-cast films (data from
279   Menzel et al.[12]) and the laboratory-scale coated films (Figure 5).

280   The amount of di-esterified CA ranged between 1% and 21% of total added CA for the solution-cast
281   starch films, whereas in the laboratory-scale coated starch films only up to 3.5% of total added CA was
282   di-esterified corresponding to a DDE of 0.01. Hence, there were large differences in di-ester content
283   between solution-cast films and laboratory-scale coated papers. In general, the formation of di-ester
284   between starch and CA was enhanced by high temperature curing. This has been described
285   previously[12,15] and has been attributed to the reaction mechanism of ester formation, where water
286   evaporation shifts the reaction towards the ester production of starch. In laboratory-scale coatings

287 fewer CA di-esters were generated, probably due to the shorter curing time (90 s) at a temperature
288 where cross-linking, i.e., ester formation, is enhanced.

289 **Pilot-scale starch coatings compared with laboratory-scale coatings**

290 The starch formulation containing 30 pph CA with an adjusted pH of 4 was scaled up in a pilot trial. In
291 addition, the starch formulation contained 87 pph platy kaolin filler Barrisurf LX (Imerys, Cornwall, UK)
292 and nano-sized clay filler Cloisite Na+ (Southern Clay Products Inc., Gonzales, Texas, US) at a
293 concentration of 3 pph. These commercial fillers were used to further improve barrier properties, e.g.
294 WVTR. The usage of the natural montmorillonite is described in detail elsewhere [27] and was not further
295 taken into account for molecular characterization of starch. The pilot trial included both single and
296 double layers on greaseproof paper.

297 *Scanning electron microscopy images of coating surface morphology*

298 Scanning electron microscopy images were taken to study the surface morphology and coverage of the
299 carrier paper and the occurrence of pinholes and cracks. Single pilot-scale coatings (Figure 6c) had quite
300 a smooth surface with a visible underlying fiber structure and many round pinholes (5-30 µm), whereas
301 double coating resulted in a smoother surface with less pinholes that were partly closed (Figure 6e). In
302 comparison, the laboratory-scale coated papers prepared at pH 4 showed no pinholes and uniform
303 coverage of the carrier paper. There were no difference between non-cured coatings (Figure 6d) and
304 coatongs cured at 150 °C (Figure 6f). Pinholes in coatings can occur due to air bubbles within the starch
305 dispersion, and hence repeated efforts were made to improve the application of the coating. For
306 example, different defoamers provided by BIM Kemi were used to try to reduce air bubbles in the starch
307 dispersion, which was successful for small-scale coating but not sufficient at pilot scale (data not shown).
308 Moreover, the surface of the paper itself was not even and in a fast coating process the starch coating
309 might not fill out the unevenness as much as in a slower process, where the starch slurry can penetrate
310 into cavities or the like. Furthermore, irregularities in thickness can cause bursting of covered holes
311 during the drying process. Slower drying, i.e., at a speed of 200 and 100 m/min, or using a soft blade to
312 apply the starch did not decrease the amount of pinholes (data not shown). However, theproblem of
313 pinholes could not be fully eliminatedand will need further investigations.

314

315

316 *Molecular changes in starch in pilot-scale coatings*

317 As described above, starch was extracted from the pilot-coated papers using 0.1M NaOH solution. The
318 M_W was 7.4±0.63 x10^5 g/mol for single layer coatings and 8.3±0.42 x10^5 g/mol for double layer coatings.
319 The M_W of the pilot-scale coatings was slightly lower than that of the as-received starch material Solcoat
320 P55 (8.8x10^5 g/mol). However, there was no significant starch degradation due to acid hydrolysis in

321 pilot-scale coatings as detected by M_W measurements, which was confirmed by the molecular
322 distribution (Figure 1).

323 The pilot-scale coatings had a water solubility of 43% and 67% for the single and double layer,
324 respectively. In comparison with laboratory-scale coatings prepared at pH 4 with 68% (non-cured) and
325 74% (cured) water-soluble starch, the starch in pilot-scale coated papers showed lower solubility in
326 water.

327 The M_W in the water-soluble starch extracted from single layer pilot papers was 16.0×10^5 g/mol, while in
328 that extracted from double layer papers it was 17.3×10^5 g/mol. This was much higher than the M_W of the
329 as-received starch material (8.8×10^5 g/mol). The strong decrease (>42%) in Mw after de-esterification
330 with NaOH implies that the starch in the water-soluble fraction was highly cross-linked. However,
331 considering the water solubility of 43% (single layer) and 67% (double layer), only a part of the starch
332 was represented.

333 The DDE of the pilot coatings was 0.024 and 0.022 for the single and double layer papers, respectively,
334 corresponding to di-esterification of about 9% of added CA. Pilot-scale coated papers showed higher
335 DDE values than solution-cast films at pH 4 and laboratory-scale coated films at pH 4 (Fig. 5).

336 One reason for these structural differences between pilot-scale coatings, laboratory-scale coatings, and
337 solution-cast films could be the extreme differences in the drying process. In the industrial pilot-scale
338 plant, the coated paper runs with a speed of 400m/min through 4 m long infrared dryers with high
339 energy output and a nominal evaporation rate of 673kg/m/h. This first drying process is very short (4 s)
340 and high-temperature (150 °C), followed by drying hoods at 65 °C for about 12 s. As the coated paper is
341 heated rapidly and water evaporates within seconds in the air infrared dryers, this results in large
342 differences in film formation, as seen in the microstructure revealed by the scanning electron
343 microscopy images (Figure 6), with e.g., pinholes and uneven surface compared with laboratory-scale
344 coatings. In addition, chemical reactions such as cross-linking and hydrolysis of starch by CA are affected.
345 The high energy output of the infrared dryers promoted cross-linking in the starch coating but no
346 hydrolysis occurred, probably due to the pH being adjusted to 4.

347

Water vapor transmission rate of pilot-scale coatings compared with laboratory-scale coatings

349 Barrier properties in terms of WVTR were measured in both laboratory-scale and pilot-scale coatings.
350 The results for the laboratory-scale coatings are described elsewhere[15] and were used here for
351 comparison with the barrier properties of pilot-scale coatings. The pilot-scale coatings had a WVTR of 77
352 and 44 g/(m² 24h) for single and double layers, respectively. As expected, higher coat weight increased
353 the barrier to water vapor movement.

354 However, the laboratory-scale coated papers showed better barrier properties, with WVTR values of 16
355 to 41 g/(m² 24h). One explanation could be the application of the coating, i.e. the evenness of the coat

356 weight and pinholes. In laboratory-scale coating, the starch solution was metered with a wire-wound
357 rod whereas at pilot scale a blade was used to meter out the coating. The latter could have resulted in
358 some compression of the carrier paper, causing slightly different patterns and coat weight variations
359 between ridges and troughs on the paper. Another reason could be shear differences beneath the blade,
360 leading to orientation of particles, aggregation and the creation of pinholes, as seen in pilot-scale
361 coatings (Figure 6). Hence, the laboratory-scale coated papers had slightly higher barrier properties in
362 terms of WVTR. Such differences in transmission when conditions are scaled up have been described
363 previously and attributed to lower coat weight due to a lower solids content in coating formulations on
364 pilot scale.[28]

365

CONCLUSIONS

367 It proved possible to extract and analyze starch from coatings on a carrier material consisting of paper.
368 There were large differences in the molecular structure of starch between solution-cast films,
369 laboratory-scale coatings and pilot-scale coatings, as evidenced by changes in molecular distribution,
370 M_W, and degree of di-esterification. Laboratory-scale coatings showed no significant hydrolysis of starch
371 and a lower degree of cross-linking of starch by CA compared with solution-cast films. On scaling up to
372 an industrial pilot trial, starch coatings showed no strong hydrolysis. The degree of di-esterification was
373 higher in pilot-scale coated papers compared with laboratory-scale coated papers and solution-cast
374 films prepared at the same pH. It was shown that cross-linking reactions between starch and CA were
375 initiated in the pilot-scale coatings even though the drying period was very short, but with a high
376 evaporation rate than in laboratory conditions. Furthermore, laboratory-scale coatings had a smoother
377 surface morphology due to more gentle coating application compared with pilot-scale application and
378 had better barrier properties against water vapor. Thus starch structure was differently influenced by
379 the drying technique applied and surface morphology, in turn affecting the barrier properties of the
380 coated paper. We believe that coated papers are more relevant than solution-cast films for studying
381 changes in molecular structure of starch. However, further investigations are needed to determine the
382 optimal laboratory conditions resembling industrial conditions.

383

ACKNOWLEDGEMENTS

CONTRIBUTION OF AUTHORS

Both authors participated in planning the experimental work, evaluation of the results and revising the manuscript. The first author was responsible for the majority of the analytical work and writing the manuscript. Both authors approved the submitted and final version.

REFERENCES AND NOTES

1. Freedonia. World Green Packaging Industry, http://www.reportlinker.com/p0593473-summary/World-Green-Packaging-Industry.html, 2011 (accessed March 21, 2013).
2. Reportlinker. Packaged Food Industry: Market Research Reports, Statistics and Analysis. http://www.reportlinker.com/ci02041/Packaged-Food.html (accessed November 11, 2013).
3. ; European Bioplastics/ Institute of Bioplastics and Biocomposites, EuBP market data. http://en.european-bioplastics.org/market/ (accessed November 11, 2013). 2012.
4. R. Babu, K. O'Connor and R. Seeram, *Progress in Biomaterials*, **2**, 8 (2013).
5. M. Jamshidian, E. A. Tehrany, M. Imran, M. Jacquot and S. Desobry, *Comprehensive Reviews in Food Science and Food Safety*, **9**, 552-571 (2010).
6. L. M. Pierce. PHA and bio-derived PE to drive bioplastic packaging market to 2020: study. http://www.packagingdigest.com/article/517396-PHA_and_bio_derived_PE_to_drive_bioplastic_packaging_market_to_2020_study.php (accessed November 11, 2013), 2011.
7. I. A. Wolff, H. A. Davis, J. E. Cluskey, L. J. Gundrum and C. E. Rist, *Industrial & Engineering Chemistry*, **43**, 915-919 (1951).
8. P. Parovuori, A. Hamunen, P. Forssell, K. Autio and K. Poutanen, *Starch - Stärke*, **47**, 19-23 (1995).
9. E. Olsson, M. S. Hedenqvist, C. Johansson and L. Järnström, *Carbohydrate Polymers*, **94**, 765-772 (2013).
10. M. I. Khalil, A. Hashem and A. Hebeish, *Starch - Stärke*, **47**, 394-398 (1995).
11. S. E. Rudolph and R. C. Glowaky. in *http://www.google.com/patents?id=I-41AAAAEBAJ*; U. S. Patent, Ed.; The Sherwin-Williams Company, Ohio, 1978.
12. C. Menzel, E. Olsson, T. S. Plivelic, R. Andersson, C. Johansson, R. Kuktaite, L. Järnström and K. Koch, *Carbohydrate Polymers*, **96**, 270-276 (2013).
13. B. Ghanbarzadeh, H. Almasi and A. A. Entezami, *Industrial Crops and Products*, **33**, 229-235 (2011).
14. N. Reddy and Y. Yang, *Food Chemistry*, **118**, 702-711 (2010).
15. E. Olsson, C. Menzel, C. Johansson, R. Andersson, K. Koch and L. Järnström, *Carbohydrate Polymers*, **98**, 1505-1513 (2013).
16. Å. Rindlav-Westling, M. Stading, A.-M. Hermansson and P. Gatenholm, *Carbohydrate Polymers*, **36**, 217-224 (1998).
17. R. A. Talja. in *Faculty of Agriculture and Forestry*; University of Helsinki, Helsinki, 2007.
18. Å. Rindlav-Westling and P. Gatenholm, *Biomacromolecules*, **4**, 166-172 (2003).
19. M. DuBois, K. A. Gilles, J. K. Hamilton, P. A. Rebers and F. Smith, *Analytical Chemistry*, **28**, 350-356 (1956).
20. W. R. Morrison and B. Laignelet, *Journal of Cereal Science*, **1**, 9-20 (1983).
21. A. Altskär, R. Andersson, A. Boldizar, K. Koch, M. Stading, M. Rigdahl and M. Thunwall, *Carbohydrate Polymers*, **71**, 591-597 (2008).
22. G. Graffmann, H. Domels and M. L. Sträter, *Fette, Seifen, Anstrichmittel*, **76**, 218-220 (1974).
23. H. Klaushofer, E. Berghofer and R. Pieber, *Starch - Stärke*, **31**, 259-261 (1979).

435   24.   M. Hirashima, R. Takahashi and K. Nishinari, *Food Hydrocolloids*, **19**, 909-914 (2005).

436   25.   R. E. Wing, *Starch - Stärke*, **48**, 275-279 (1996).

437   26.   Å. Rindlav, S. H. D. Hulleman and P. Gatenholm, *Carbohydrate Polymers*, **34**, 25-30 (1997).

438   27.   E. Olsson, C. Johansson and L. Järnström, *Applied clay science*(just accepted).

439   28.   H. Kjellgren, M. Gällstedt, G. Engström and L. Järnström, *Carbohydrate Polymers*, **65**, 453-460

440   (2006).

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442