

Impact of the Coating Process on the Molecular Structure of Starch-Based Barrier Coatings

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ABSTRACT: Molecular analysis of starch structure can be used to explain and predict changes in physical properties, such as water vapor and oxygen barrier properties in packaging materials. Solution casting is a widely used technique to create films from starch formulations. This study compared the molecular properties of these standard films with those of experimental coatings applied to paper in laboratory-scale and pilot-scale trials, with all three techniques using the same starch formulation. The results revealed large differences in molecular structure, i.e., cross-linking and hydrolysis, between films and coatings. The main differences were due to the shorter drying time allowed to laboratory-scale coatings and the accelerated drying process in pilot trials owing to the high energy output of infrared dryers. Furthermore, surface morphology was highly affected by the coating technique used, with a rougher surface and many pinholes occurring in pilot-scale coatings, giving lower water vapor permeability than laboratory-scale coatings. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41190.

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INTRODUCTION

There is increasing demand for green packaging materials in the world, driven by industrial growth and trends for environmentally friendly packaging.¹ The world demand for food packaging is expected to grow about 2.5% per year.² The expected production capacity of bioplastics is expected to grow fivefold from 2011 to 2016 as the largest sector in packaging.³ Hence, there have been intensive investigations on bio-based materials, especially from bio-polymers, for packaging purposes. Conventional food packaging consists of multi-layer films of synthetic plastics and adhesives to provide barrier properties, allow color printing, and bind all layers together. From an environmental point of view, it is desirable to replace these coatings with renewable types. Several bio-polymers such as starch, poly-lactic acid, and polyhydroxybutyrate can replace synthetic plastics such as polyethylene terephthalate or polystyrene plastics.^{4,5} In 2010, starch represented the second largest sector of the global bioplastic packaging market, accounting for 22.2%.⁶ Starch is a widely used bio-polymer for the production of films and coatings because of its abundance and ability to form a network structure. The possibility of using starch as a base in new materials has been extensively researched since the 1950s.⁷ Starch is commonly plasticized with glycerol to overcome its brittleness and several chemical modifications can be used to improve the

hydrophilic character of starch. Due to its structure of chains of (1→4) linked α -glucan units and numerous free hydroxyl groups, various chemical modifications such as acid hydrolysis, oxidation,⁸ cross-linking,⁹ and acetylation^{10,11} can be applied to obtain desired physical properties. Regarding barrier properties for food packaging, the most critical compounds are water vapor and oxygen, since these compounds can permeate through the packaging material and alter the food quality. In recent studies, cross-linking with citric acid (CA) has been cited as a promising additive to improve the thermal and barrier properties of starch films.^{9,12,13} In those studies, changes in molecular structure due to acid hydrolysis and cross-linking by adding CA were analyzed using solution-cast films.¹² In a study by Olsson et al.,⁹ starch films containing up to 30 pph CA reduced moisture content, diffusion coefficient, and water vapor permeability confirming previous findings.^{13,14} Molecular characterization studies on the same films confirmed that high CA content and high-temperature curing increased cross-linking reactions, but that hydrolysis of starch occurred simultaneously. To prevent severe hydrolysis of starch films at high CA content and preserve improved barrier properties at the same time, pH adjustments to the starch formulation before drying were tested. It was shown that at pH 4, starch hydrolysis was stopped, while cross-linking still occurred. In addition, gas barrier properties, i.e., oxygen and water vapor permeability, showed a minimum

at pH 4 measured on laboratory-scale coated paper based on the same starch solution and prepared under comparable drying conditions.^{9,15} However, to the best of our knowledge, there are no studies comparing the impact of the coating process on the molecular structure of starch coated on paper or paperboard, either in the laboratory or at pilot scale, relative to solution-cast films.

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

The objectives of this study were therefore: (1) to find suitable methods to analyze the molecular structure of starch in paper coatings, (2) to determine the impact of the coating process parameters on the molecular and barrier properties of starch-based coatings, and (3) to compare the molecular structure of solution-cast starch films and laboratory-scale coated papers with that of industrially produced starch coatings from a pilot trial. Experimental parameters for the pilot trial were chosen according to a previous study,¹⁵ where laboratory-scale coated papers showed a minimum in water vapor transmission rate (WVTR) and no hydrolysis when the pH was kept at 4 for a CA-starch formulation. That study showed that molecular changes in solution-cast films cannot be directly related to barrier properties that are generally measured on coated papers. There were large differences in molecular structure between solution-cast films and laboratory-scale coated papers. No hydrolysis was detectable due to the shorter drying time applied to the laboratory-scale coatings. The pilot-scale coatings also showed no hydrolysis, but demonstrated a higher degree of cross-linking compared with the laboratory-scale coated papers and solution-cast films. At pilot scale, the drying process is accelerated by the high energy output of infrared dryers, which evaporates the water in a very short time and initiates the ester-

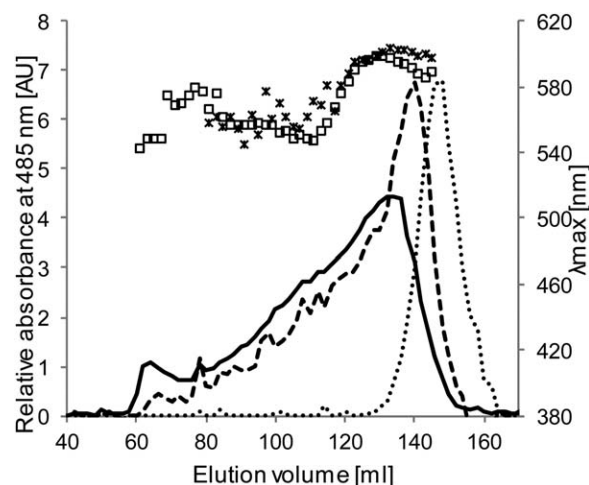


Figure 1. Size-exclusion chromatogram of as-received starch Solcoat P55 (—, □), starch from double-coated paper in pilot scale (---, ×) and uncoated carrier paper (... ..) dissolved in 0.1M NaOH. (lines: glucose concentration, dots: wavelength at maximum absorbance λ_{\max}).

ification and finally cross-linking reaction. The higher water vapor permeability in pilot-scale coatings has been attributed to a rougher and more uneven surface and large visible pinholes compared with laboratory-scale coatings due to the coating technique applied.

EXPERIMENTAL

Materials

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

Preparation of Starch Films and Starch Coatings

Solution-Cast Starch Films. The preparation of solution-cast starch films is described in detail elsewhere.⁹ In brief, a 10% (w/w) starch (Solcoat 155) solution was gelatinized in a boiling water bath, cooled to room temperature, and 30 parts CA per

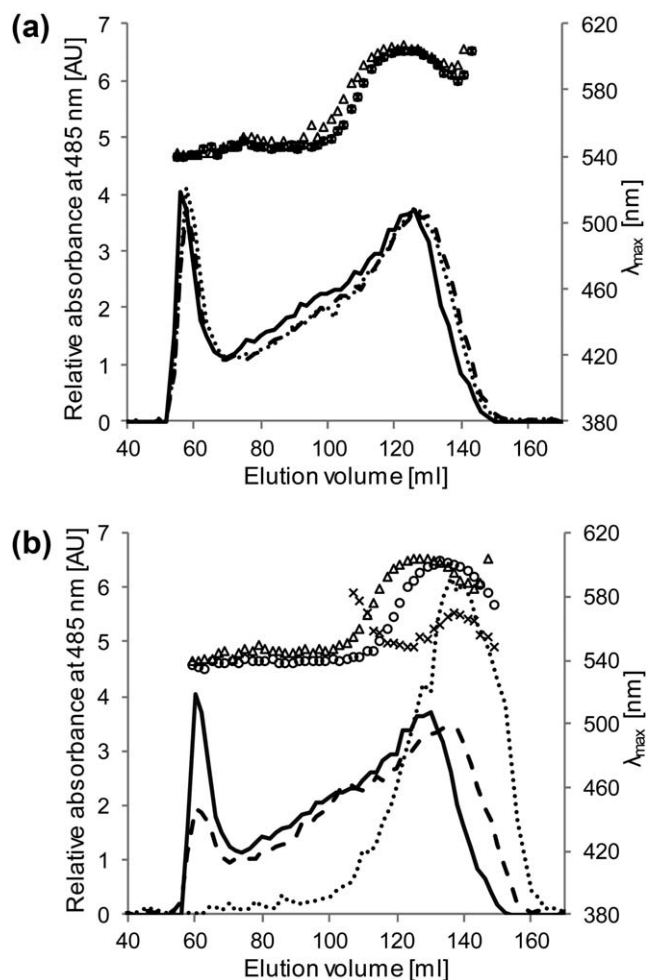


Figure 2. Molecular distribution of amylose and amylopectin in (a) laboratory-scale coated papers prepared at pH 2, non-cured (....., ×) and cured at 150°C (---, ○) and as-received starch Solcoat 155 (—, Δ); and (b) solution-cast starch films at pH 2 (....., ×), pH 4 (---, ○) and as-received starch Solcoat 155 (—, Δ) cured at 150°C (lines: glucose concentration, dots: wavelength at maximum absorbance λ_{\max}).

100 parts of dry starch (pph) were added. The CA-containing starch solution was then adjusted to different pH values (2, 4, and 6.5) using 10M NaOH solution, cast in Petri dishes and dried at 70°C for 5 h. The dried solution-cast films were heat-treated (cured) for 10 min at 150°C.

Laboratory-Scale Starch Coatings on Paper. The laboratory-scale starch coatings were prepared according to Olsson et al.¹⁵ The pH-adjusted starch (Solcoat 155) solutions described above were coated in double layers on Super Perga WS Parchment 70 g/m² paper (Nordic Paper, Greåker, Norway) using a bench coater and a wire-wound bar (K202 Control Coater, RK Coat Instrument Ltd., Royston, UK). The first layer was dried before applying the second layer and both coated layers were dried at either 70°C or 150°C for 90 s. The coat weight was measured according to Olsson et al.¹⁵ In brief, the difference in weight between coated and uncoated papers was measured after conditioning at 23°C and 50% RH for at least 24 h. The resulting coat weight was between 15 and 18 g/m².

Pilot-Scale Starch Coatings on Paper. Pilot-scale coating was carried out using an industrial machine (UMV Coating Systems AB, Säffle, Sweden) and a starch (Solcoat P55) formulation with pH adjusted to 4. The coatings were applied either as single or double layers. The machine parameters were: machine speed 400 m/min, coating technique hard tip, drying with infrared dryer at 150°C, followed by 60°C at 35% RH, and a nominal evaporation rate of 673 kg/m/h. The starch formulation consisted of 100 pph starch and 30 pph CA, adjusted to pH 4 with NaOH and 0.01% (w/w) defoamer BIM 7640 (BIM Kemi Sweden AB). Two commonly used and well-studied industrial clay fillers, 87 pph kaolin filler (Barrisurf LXTM, Imerys) and 3 pph nanosized clay filler (Cloisite Na⁺TM, Southern Clay Products Inc.), were added to improve barrier properties and develop a renewable starch formulation for industrial usage. The resulting coat weight was 6 and 11 g/m² for single and double coatings, respectively, on greaseproof paper Super Perga WS Parchment 70 g/m² (Nordic Paper Greåker, Norway).

Extraction of Starch from the Coated Paper

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

Molecular Characterization of Amylose and Amylopectin

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

Determination of Weight-Average Molecular Weight (M_w)

Weight-average molecular weight (M_w) was measured on solution-cast starch films and on extracted starch from coatings, which were then dissolved in either 0.1M NaOH solution or distilled water. Therefore, about 25 mg solution-cast films or 100 mg starch-coated paper were suspended in 5 mL of the respective solvent for 2 h and gently stirred using a magnetic stirrer. The NaOH suspensions were kept at room temperature, while the water suspensions were heated to 70°C in a water bath to dissolve the starch. The solutions were filtered through a 0.45 μm filter and directly injected (75 μL) into a high-

performance size-exclusion chromatography (HPSEC) system coupled with a multi-angle laser-light scattering (MALLS) detector and a refractive index (RI) detector, as described elsewhere.¹² Furthermore, a 950- μ L aliquot of the filtered water suspension was treated with 50 μ L 2M NaOH to detect possible changes in M_W due to expected cross-linkage formation between CA and starch. The experiments were performed in duplicate.

Solubility in Water

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

Titration with Copper (II)-Sulfate for CA Di-Ester Determination

Citric acid di-esters were determined according to the complexometric titration method of CA with copper(II)-ions described by Graffmann et al.,^{22,23} with small modifications as described elsewhere.¹² In brief, 300 mg solution-cast starch film or 1 g starch-coated paper was weighed into a beaker and two different treatments, direct titration and titration after hydrolysis, were carried out. Starch ester bonds were hydrolyzed using 50 mL 0.1M KOH (pH >12). In both treatments, a borax/boric acid buffer (pH 8.5) was added and the starch samples were titrated with 0.02M copper(II)-sulfate solution. The content of 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 $\times 100$.

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 0.1M NaOH, stirred for 20 min and subsequently filtered through a 0.45 μ m 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 (1M

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 0.1M 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 and cured at 150°C). However, with high-temperature curing (150°C) of the solution-cast starch films, the first eluting peak corresponding to amylopectin was strongly affected at different pH levels due to starch degradation [Figure 2(b)]. For the laboratory-scale coated starch films no degradation of starch molecules was detected and hence no hydrolysis due to CA had taken place compared with the as-received starch [Figure 2(a)]. One explanation could be differences in the drying process of the coatings and films, as the curing time to produce laboratory-scale coated starch papers was substantially shorter (90 s) than that for solution-cast films (10 min). In addition, it is reasonable to believe that heating the coated papers to the same temperature as the solution-cast films took a longer time due to the thickness of the material. It has been shown previously that high temperature promotes acid hydrolysis^{12,24,25} and that different drying conditions influence film formation and molecular structure in starch films.^{16,26} Hence, during the shorter drying time for the starch coatings, less starch was degraded compared with in the solution-cast films. It is important to consider the drying method applied to coatings and cast films in order to predict molecular changes in solution-cast films coated on paper in the laboratory, as well as coatings prepared under industrial conditions.

M_W Determination in 0.1M NaOH and Water. Starch from solution-cast films and laboratory-scale coated films were dissolved in 0.1M NaOH to determine M_W of the de-esterified starch molecules (Figure 3). Solution-cast films as described previously by Olsson et al.¹⁵ were used as reference. The M_W of starch from coatings was between 6.3 and 8.0 $\times 10^6$ g/mol for non-cured and 150°C cured coatings, compared with 8.8 $\times 10^6$ g/mol for as-received starch. There were no significant differences (*t*-test, $P > 0.05$) between coatings prepared in the different

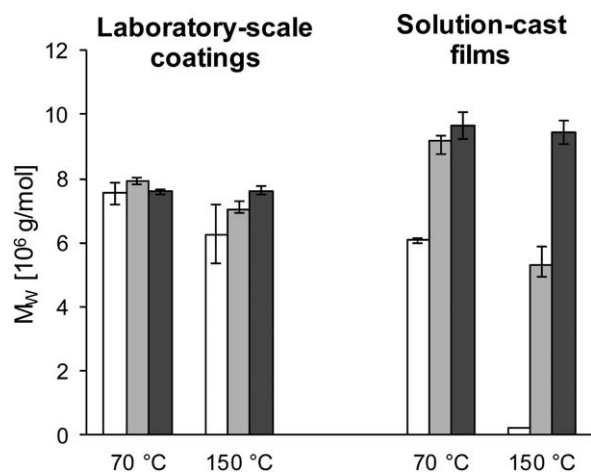


Figure 3. Weight-average molecular weight (M_w) in $0.1M$ NaOH of solution-cast starch films and laboratory-scale coated papers prepared at different pH (white—pH 2, light gray—pH 4, dark gray—pH 6.5) non-cured (70°C) and cured at 150°C . Error bars indicate standard deviation.

conditions, i.e., neither pH nor high-temperature curing affected M_w of the starch applied as a coating on paper. This is in agreement with the results from molecular analysis of amylose and amylopectin showing no degradation of starch in laboratory-scale coated paper [Figure 2(a)]. However, solution-cast starch films were strongly affected by pH and high-temperature curing, e.g., a decrease in M_w with decreasing pH (Figure 3). Adjustment of the pH to higher values prevented acid hydrolysis even in cured films, as shown in a previous study.¹⁵

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

Laboratory-scale coating on paper showed higher water solubility (63–80%) than the reference solution-cast starch films (16–48%, data from Olsson et al.¹⁵). This could be due to a lower degree of cross-linking of starch molecules by CA in the laboratory-scale starch coatings compared with the solution-cast starch films, resulting in higher water solubility.

Table I. Weight-Average Molecular Weight (M_w , $\times 10^6$ g/mol) in Water and After Subsequent Treatment with NaOH (Water + NaOH) of Lab Coatings and Solution-Cast Starch Films (Data for Solution-Cast Films Taken from Olsson et al.¹⁵), Non-Cured and Cured at 150°C (Mean of Duplicates \pm Standard Deviation)

Sample	M_w in water		M_w in water + NaOH	
	Non-cured, 70°C	Cured at 150°C	Non-cured, 70°C	Cured at 150°C
Lab coatings				
pH 2	5.5 ± 0.03	5.3 ± 0.21	4.2 ± 0.01	4.0 ± 0.03
pH 4	7.3 ± 0.14	7.4 ± 0.18	6.9 ± 0.34	6.2 ± 0.01
pH 6.5	8.6 ± 0.07	8.7 ± 0.21	8.1 ± 0.11	7.7 ± 0.67
Solution-cast films				
pH 2	0.4 ± 0.11	0.4 ± 0.01	0.3 ± 0.01	0.1 ± 0.03
pH 4	9.5 ± 0.07	0.2 ± 0.01	8.7 ± 0.22	0.2 ± 0.06
pH 6.5	10.3 ± 0.09	10.2 ± 0.60	10.1 ± 0.66	9.5 ± 0.51

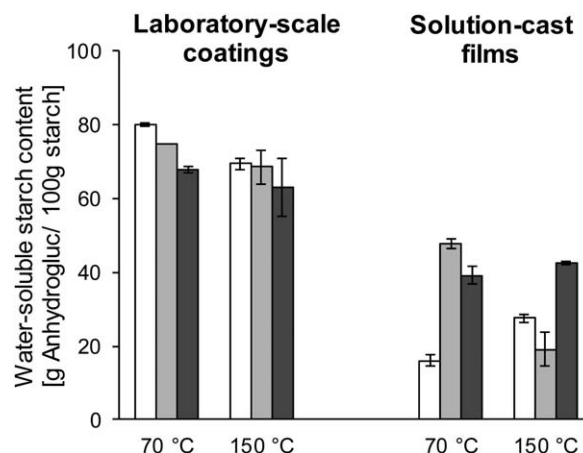


Figure 4. Water-soluble starch content of solution-cast starch films and laboratory-scale coated papers prepared at different pH (white—pH 2, light gray—pH 4, dark gray—pH 6.5), non-cured (70°C) and cured at 150°C . Error bars indicate standard deviation.

The M_w of the water-soluble starch extracted from laboratory-scale coated papers was lowest for coatings prepared at pH 2 (5.5×10^6 g/mol) and increased with increasing pH (Table I). There was no significant change in M_w when coatings were cured at high temperature (150°C). The M_w of water-soluble starch was similar to that of de-esterified starch in NaOH (Figure 3), as anticipated from the high water solubility. Only coatings prepared at pH 2 had a slightly lower M_w in water (Table I), although water alone also gave the highest water solubility.

Cross-linking of starch by CA was detectable as a change in M_w of the water-soluble starch after subsequent treatment with NaOH which induced hydrolysis of the ester bonds between one CA molecule and two starch molecules and hence reduced M_w (Table I). The laboratory-scale coated papers prepared at pH 2 showed the highest M_w decrease (23% non-cured, 26% cured) after NaOH treatment of the water-soluble starch. The M_w decrease was lower for laboratory-scale coatings prepared at pH 4 (6% non-cured, 16% cured) and pH 6.5 (6% non-cured, 12% cured), indicating fewer CA cross-linkages in the water-

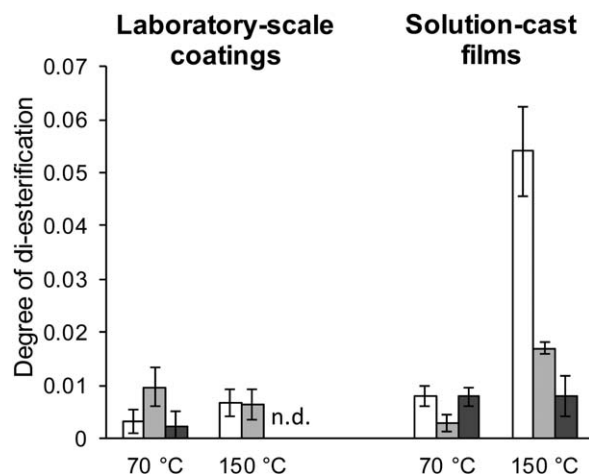


Figure 5. Degree of di-esterification of solution-cast starch films and laboratory-scale coated papers prepared at different pH and non-cured (70 °C) or cured (150 °C). Error bars indicate standard deviation of triplicates (n.d., not detectable).

soluble starch extract. The cross-linking reaction, which is basically Fischer esterification, is catalyzed at low pH explaining the larger decrease in M_w at pH 2. High-temperature curing of the coatings resulted in slightly higher M_w decreases after NaOH treatment and hence a higher degree of cross-linking. In contrast, M_w before and after de-esterification of water-soluble starch from solution-cast films was highly affected by both pH-adjustment and curing, resulting in highly cross-linked films at pH 2 (M_w decrease 19%) and high temperature (M_w decrease 85%), as described and discussed in previous reports.¹⁵

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

Citric Acid Di-Ester Determination in Solution-Cast Starch Films and Laboratory-Scale Coated Papers. As described in previous reports,¹² the titration of CA with copper (II)-sulfate can detect CA and mono-esterified CA molecules. Hence, titration before and after hydrolysis shows the amount of CA molecules that are di-esterified and potentially cross-linked between different starch molecules. The CA di-ester content was expressed in terms of degree of di-esterification (DDE) for the solution-cast films (data from Menzel et al.¹²) and the laboratory-scale coated papers (Figure 5).

The amount of di-esterified CA ranged between 1% and 21% of total added CA for the solution-cast starch films, whereas in the laboratory-scale coated papers only up to 3.5% of total added CA was di-esterified corresponding to a DDE of 0.01.

Hence, there were large differences in di-ester content between solution-cast films and laboratory-scale coated papers. In general, the formation of di-ester between starch and CA was enhanced by high-temperature curing. This has been described previously^{12,15} and has been attributed to the reaction mechanism of ester formation, where water evaporation shifts the reaction towards the ester production of starch. In laboratory-scale coatings fewer CA di-esters were generated, probably due to the shorter curing time (90 s) at a temperature where cross-linking, i.e., ester formation, is enhanced.

Pilot-Scale Starch Coatings Compared with Laboratory-Scale Coatings

The starch formulation containing 30 pph CA with an adjusted pH of 4 was scaled up in a pilot trial. In addition, the starch formulation contained 87 pph platy kaolin filler Barrisurf LX (Imerys, Cornwall, UK) and nanosized clay filler Cloisite Na+ (Southern Clay Products Inc., Gonzales, Texas, US) at a concentration of 3 pph. These commercial fillers were used to further improve barrier properties, e.g., WVTR. The usage of the natural montmorillonite is described in detail elsewhere²⁷ and was not further taken into account for molecular characterization of starch. The pilot trial included both single and double layers on greaseproof paper.

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

Molecular Changes in Starch in Pilot-Scale Coatings. As described above, starch was extracted from the pilot-coated papers using 0.1M NaOH solution. The M_w was $7.4 \pm 0.63 \times 10^5$ g/mol for single layer coatings and $8.3 \pm 0.42 \times 10^5$ g/mol for double layer coatings. The M_w of the pilot-scale coatings

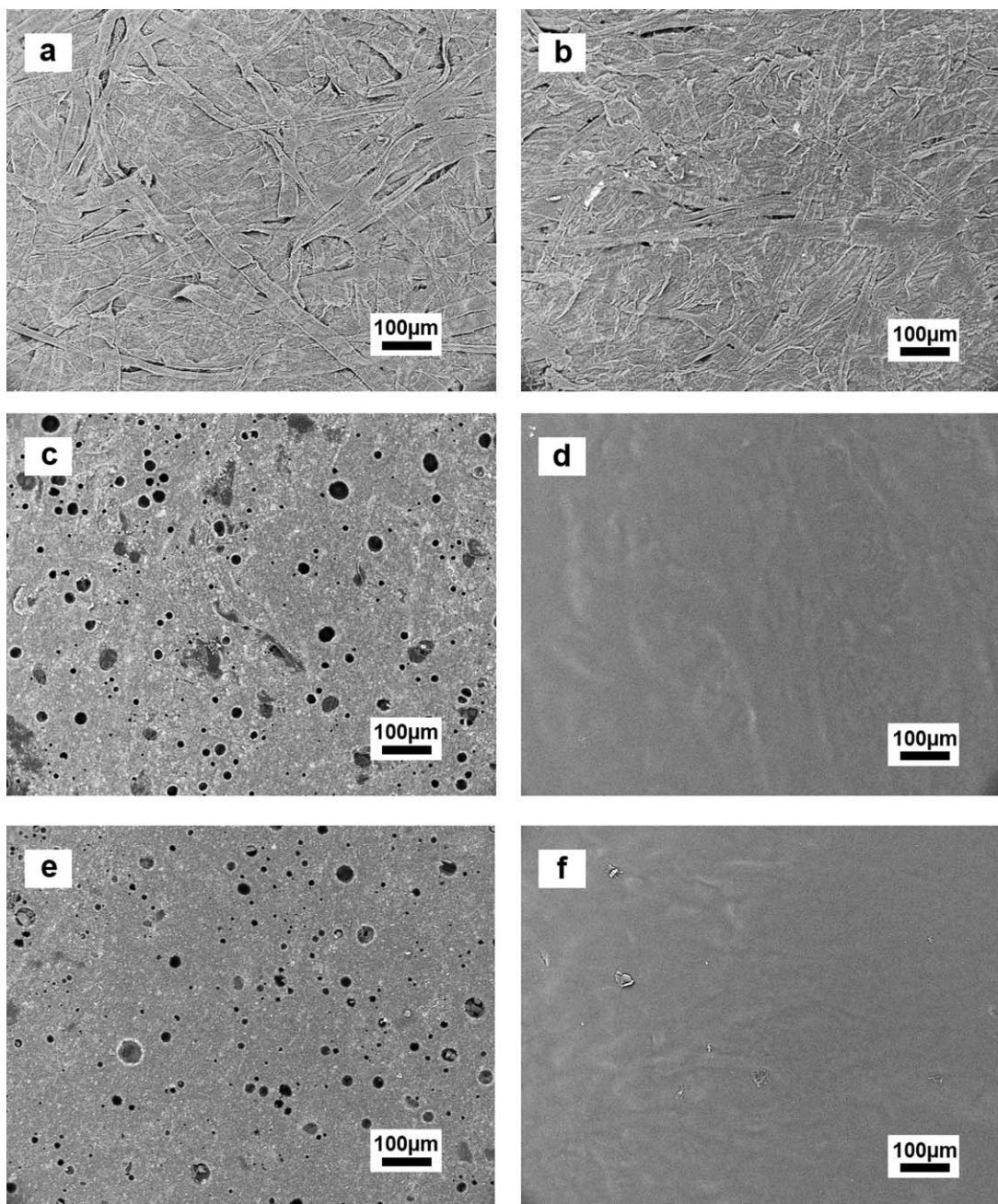


Figure 6. Scanning electron microscopy (SEM) images of: uncoated carrier paper in (a) the pilot trial and (b) the laboratory-scale experiment; coated pilot paper at pH 4 in (c) a single layer and (e) a double layer; and laboratory-scale coatings at pH 4 with (d) no curing and (f) curing at 150°C.

was slightly lower than that of the as-received starch material Solcoat P55 (8.8×10^5 g/mol). However, there was no significant starch degradation due to acid hydrolysis in pilot-scale coatings as detected by M_w measurements, which was confirmed by the molecular distribution (Figure 1).

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

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

The DDE of the pilot coatings was 0.024 and 0.022 for the single and double layer papers, respectively, corresponding to

di-esterification of about 9% of added CA. Pilot-scale coated papers showed higher DDE values than solution-cast films at pH 4 and laboratory-scale coated films at pH 4 (Figure 5).

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

Water Vapor Transmission Rate of Pilot-Scale Coatings Compared with Laboratory-Scale Coatings. Barrier properties in terms of WVTR were measured in both laboratory-scale and pilot-scale coatings. The results for the laboratory-scale coatings are described elsewhere¹⁵ and were used here for comparison with the barrier properties of pilot-scale coatings. The pilot-scale coatings had a WVTR of 77 and 44 g/(m² 24h) for single and double layers, respectively. As expected, higher coat weight increased the barrier to water vapor movement.

However, the laboratory-scale coated papers showed better barrier properties, with WVTR values of 16–41 g/(m² 24h). One explanation could be the application of the coating, i.e., the evenness of the coat weight and pinholes. In laboratory-scale coating, the starch solution was metered with a wire-wound rod whereas at pilot scale a blade was used to meter out the coating. The latter could have resulted in some compression of the carrier paper, causing slightly different patterns and coat weight variations between ridges and troughs on the paper. Another reason could be shear differences beneath the blade, leading to orientation of particles, aggregation and the creation of pinholes, as seen in pilot-scale coatings (Figure 6). Hence, the laboratory-scale coated papers had slightly higher barrier properties in terms of WVTR. Such differences in transmission when conditions are scaled up have been described previously and attributed to lower coat weight due to a lower solids content in coating formulations on pilot scale.²⁸

CONCLUSIONS

It proved possible to extract and analyze starch from coatings on a carrier material consisting of paper. There were large differences in the molecular structure of starch between solution-cast films, laboratory-scale coatings and pilot-scale coatings, as evidenced by changes in molecular distribution, M_{w5} and degree of di-esterification. Laboratory-scale coatings showed no signifi-

cant hydrolysis of starch and a lower degree of cross-linking of starch by CA compared with solution-cast films. On scaling up to an industrial pilot trial, starch coatings showed no strong hydrolysis. The degree of di-esterification was higher in pilot-scale coated papers compared with laboratory-scale coated papers and solution-cast films prepared at the same pH. It was shown that cross-linking reactions between starch and CA were initiated in the pilot-scale coatings even though the drying period was very short, but with a high evaporation rate than in laboratory conditions. Furthermore, laboratory-scale coatings had a smoother surface morphology due to more gentle coating application compared with pilot-scale application and had better barrier properties against water vapor. Thus starch structure was differently influenced by the drying technique applied and surface morphology, in turn affecting the barrier properties of the coated paper. We believe that coated papers are more relevant than solution-cast films for studying changes in molecular structure of starch. However, further investigations are needed to determine the optimal laboratory conditions resembling industrial conditions.

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.

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