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The effect of pH on hydrolysis, cross-linking and barrier properties of starch barriers containing citric acid

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ABSTRACT

Citric acid cross-linking of starch for e.g. food packaging applications has been intensely studied during the last decade as a method of producing water-insensitive renewable barrier coatings. We managed to improve a starch formulation containing citric acid as cross-linking agent for industrial paper coating applications by adjusting the pH of the starch solution. The described starch formulations exhibited both cross-linking of starch by citric acid as well as satisfactory barrier properties, e.g. fairly low OTR values at 50% RH that are comparable with EVOH. Furthermore, it has been shown that barrier properties of coated papers with different solution pH were correlated to molecular changes in starch showing both hydrolysis and cross-linking of starch molecules in the presence of citric acid. Hydrolysis was shown to be almost completely hindered at solution pH ≥ 4 at curing temperatures $\leq 105\,^{\circ}C$ and at pH ≥ 5 at curing temperatures $\leq 150\,^{\circ}C$, whereas cross-linking still occurred to some extent at pH ≤ 6.5 and drying temperatures as low as $70\,^{\circ}C$. Coated papers showed a minimum in water vapor transmission rate at pH 4 of the starch coating solution, corresponding to the point where hydrolysis was effectively hindered but where a significant degree of cross-linking still occurred.

1. Introduction

The search for renewable materials to replace synthetic oil-based materials as barriers for consumer packages is an intense research field. Thermoplastic starch, TPS, is one of the most promising biopolymer materials to be used in packaging applications since it is renewable, is abundant at low cost, and is fully biodegradable. However, the inherent water sensitivity of TPS is a major problem limiting its use as a barrier material. Plasticization lowers the glass transition temperature, T_g, and increases the molecular mobility in the films. Water is one of the most efficient plasticizers for TPS (Mathew & Dufresne, 2002). Since starch and many of its plasticizers are hygroscopic, which means that the moisture content in the films increases with increasing relative humidity, RH, the barrier properties are significantly reduced with increasing RH (Forssell, Lahtinen, Lahelin, & Myllarinen, 2002; Gaudin, Lourdin, Forssell, & Colonna, 2000).

Recent research regarding TPS has focused on how to better utilize its potential as a barrier by decreasing its water sensitivity. Strategies being utilized involve blending with natural (Gaspar, Benko, Dogossy, Reczey, & Czigany, 2005) or synthetic (Shi et al., 2008) polymers, the incorporation of inorganic filler such as clay (Magalhães & Andrade, 2009), incorporation of organic fillers based on cellulose (Lopez-Rubio et al., 2007; Svagan, Hedenqvist, & Berglund, 2009), or starch (Habibi & Dufresne, 2008), modifying the starch (Jonhed, Andersson, & Jarnstrom, 2008; Yu, Chang, & Ma, 2010), studying different plasticizers and plasticizer concentrations (Huang, Yu, & Ma, 2006; Lourdin, Coignard, Bizot, & Colonna, 1997; Olsson, Hedenqvist, Johansson, & Järnström, 2013), using combinations of plasticizers (Shi et al., 2007) and by cross-linking the starch (Yoon, Chough, & Park, 2006) for instance with citric acid, CA (Menzel et al., 2013). CA is generally recognized as safe according to FDA and EFSA and is thus suitable for use in food packaging applications. The incorporation of CA and other natural polycarboxylic acids into films based on renewable materials has been the subject of recent research since CA has been shown to improve the mechanical and barrier properties of such materials, which has mainly been attributed to cross-linking (Dastidar & Netravali, 2012; Ning, Xingxiang, Na, & Jianming, 2010; Olivato, Grossmann, Bilck, & Yamashita, 2012; Wang, Yu, Chang, & Ma, 2007). Cross-linking of polysaccharide materials such as thermoplastic starch (Shi et al., 2007), paper (Yang, Xu, & Wang, 1996), cellulose derivatives (Coma, Sebti, Pardon, Pichavant, & Deschamps, 2003), starch granules (Xie

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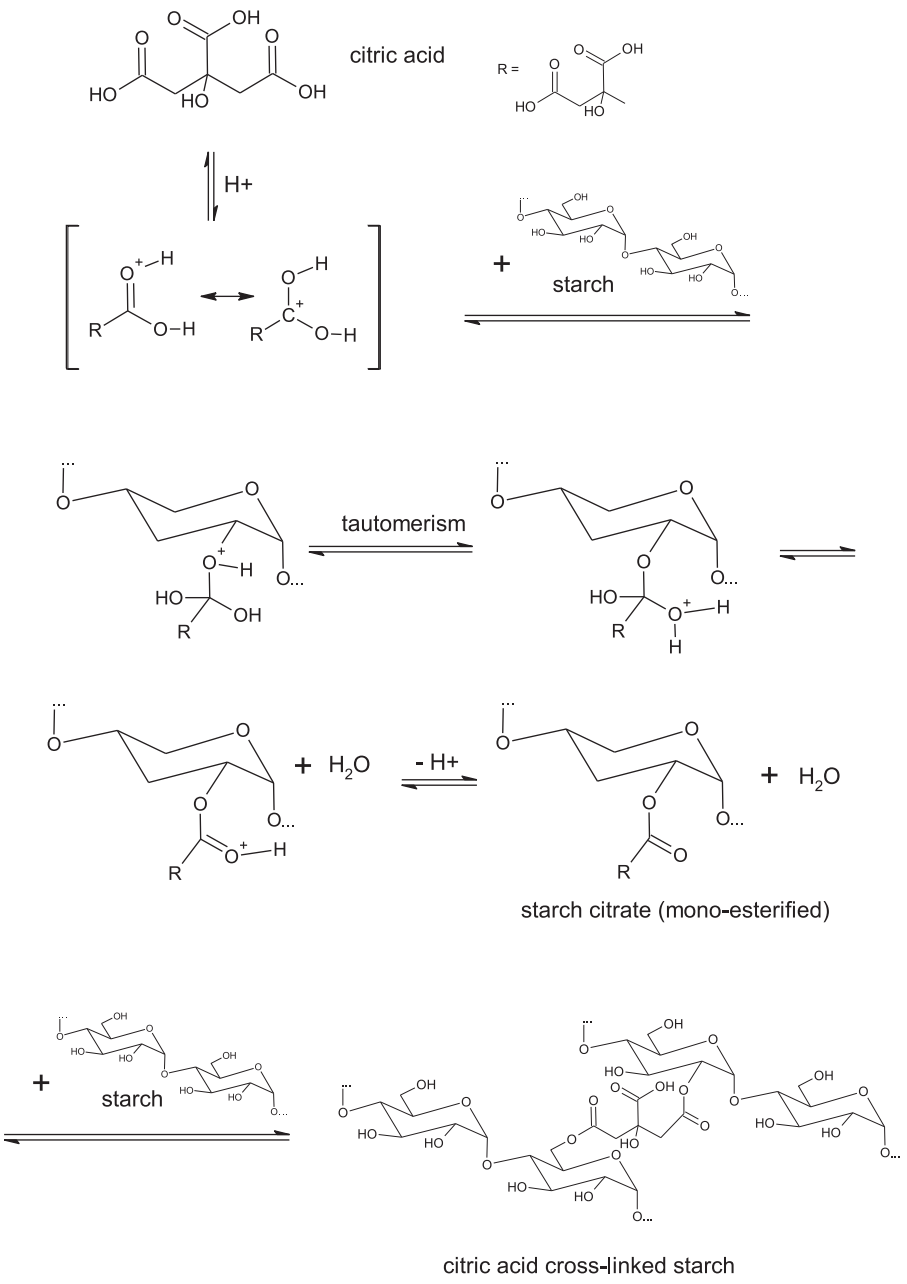

Fig. 1. Schematic illustration of the acid-catalyzed esterification of citric acid and starch to starch citrate (mono-esterified) and a possible structure of citric acid cross-linked starch.

& Liu, 2004), and cotton fibers (Andrews & Reinhardt, 1996) has been shown to occur with different polycarboxylic acids such as butanetetracarboxylic (Yang et al., 1996), malic, tartaric, malonic, glutaric, succinic, adipic and citric acid (Seidel et al., 2001; Shi et al., 2007) with or without a catalyst such as sodium hypophosphite (Reddy & Yang, 2010) or dihydrogen sodium phosphate (Wing, 1996) at elevated temperatures. The addition of CA to starch has previously shown to give solution cast films a reduced water-sensitivity and improved barrier properties, both by a reduction of the diffusion coefficient of water and by a reduction of the moisture content of the films (Olsson et al., 2013; Ghanbarzadeh, Almasi, & Entezami, 2011). The reaction mechanism for the cross-linking, i.e. inter molecular di-ester formation, is the well-known Fischer-esterification between the carboxylic acid groups of CA and the hydroxyl groups in starch occurring twice within the same CA molecule. The formation of an ester-bond can be catalyzed by reducing the pH or by adding Lewis acids. The schematic reaction mechanism is shown in Fig. 1. In most previous studies, very high reaction temperature in most cases well above 100 °C was used to initiate cross-linking (Dastidar & Netravali, 2012; Ning et al., 2010; Olivato et al., 2012; Shi et al., 2007; Wang et al., 2007; Wing, 1996). However, in a recent study, it was possible to achieve significant cross-linking at low temperature (70 °C) if the amount of CA was high. The reaction efficiency of the CA was low in that case and only a very small fraction of the added CA took part in the cross-linking reaction (Menzel et al., 2013). Nevertheless, unreacted CA and monoesterified CA can work as a plasticizer for the starch as seen i.e. by a reduction in the T_g (Menzel et al., 2013). It has even been shown that CA can be used as the sole plasticizer for starch (Olsson et al., 2013) and increase the elongation at break for starch-poly (vinyl alcohol) blends. The increase in elongation is stronger than for glycerol as plasticizer (Yoon et al., 2006). It has also been

shown to increase the elongation at break in combination with other plasticizers such as glycerol for starch (Jiugao, Ning, & Xiaofei, 2005; Ning et al., 2010; Wang et al., 2007) or starch-poly (vinyl alcohol) blends (Ning et al., 2010; Shi et al., 2008; Wang et al., 2007). It has also been shown that CA reduces the T_g (Menzel et al., 2013).

In excess water, CA can promote starch fragmentation, the onset of gelatinization and acid hydrolysis. Acid hydrolysis during gelatinization is promoted by both an increase of CA content and a reduction in pH (Campbell & Briant, 1957; Hansuld & Briant, 1954; Hirashima, Takahashi, & Nishinari, 2005; Yamada, Morimoto, & Hisamatsu, 1986). Cleavage of glycosidic linkages in starch by acid hydrolysis involves both the protonation of the glycosidic oxygen and the addition of a water molecule to yield the reducing sugar end group. However, the addition of acid to a starch formulation does not automatically lead to hydrolysis. For acid hydrolysis to take place with carboxylic acids, both low pH and high temperature are needed, as demonstrated in a study by Hirashima et al. (2005) where the addition of acids before and after gelatinization was studied, and it was found that no hydrolysis occurred without sufficient temperature (Hirashima et al., 2005). It has been suggested that it is possible to produce CA cross-linked starch films without excessive hydrolysis by pre-drying at a low temperature, thereby removing most of the water before raising the temperature (Wing, 1996). However, a recent study showed that exposure to high temperature, (150 °C) of starch films with a high CA content (30 pph) resulted in severe hydrolysis even in pre-dried films (Menzel et al., 2013).

In the present work, the effect of pH and reaction temperature (curing) on material properties of CA containing starch films was examined. A high amount of CA was used both for the improved barrier properties and the higher reaction kinetics seen in previous studies (Menzel et al., 2013; Olsson et al., 2013) Factors such as molecular weight and degree of cross-linking were linked to the barrier properties, i.e. water vapor and oxygen transmission rates.

2. Materials and methods

2.1. Materials

The starch films and coatings consisted of a hydroxypropylated and oxidized potato starch (Solcoat 155) (with an amylose content of 21%, a degree of substitution of hydroxypropyl groups 0.11 and an average 0.01 carboxylic acid groups per anhydroglucose unit (Jonhed et al., 2008)) generously supplied by Solam (Kristianstad, Sweden), and CA (anhydrous citric acid, Puriss, Sigma–Aldrich Inc., St. Louis, USA), added at a concentration of 30 parts per hundred, pph based on the dry weight of starch. The initial pH of the starch solution with 30 pph CA was approximately 2 and it was adjusted to 3, 4, 5, and 6.5 with 40 wt% NaOH.

The starch gelatinization, film casting and paper coating were performed according to Olsson et al. (2013). In brief, the starch was gelatinized in a boiling water bath under vigorous stirring for 45 min. CA was added to the gelatinized starch after it had cooled to room temperature and the pH was adjusted with NaOH. The films used for molecular characterization were cast in Petri dishes and dried at 70 °C for 5 h with or without subsequent curing at 105 or 150 °C for 10 min. A paper substrate, Super Perga WS Parchment, 50 g/m^2 (Nordic Paper Greåker, Norway), was coated and used for the subsequent evaluation of barrier properties. This paper is a greaseproof paper with very low porosity. It has a specified air permeance according to SCAN P26 of 0.01 nm Pa s according to the supplier. The coatings were applied in two layers with a wire-wound bar, 0.31 mm in wire diameter, using a bench coater (K202 Control Coater, RK Coat Instruments Ltd., Royston, UK) at a coating speed of 6 m/min. The coated sheets were subsequently dried in an oven for 90 s at 70, 105 or 150 °C.

2.2. Multi-angle laser-light scattering for the determination of weight-average molecular weight (M_W)

2.2.1. M_W after de-esterification

Starch film samples were dissolved in 0.1 M NaOH to ensure that starch citrate esters were completely de-esterified and that only molecular changes in starch molecules were measured. The determination of M_W is described elsewhere (Menzel et al., 2013) and was carried out using high-performance size-exclusion chromatography (HPSEC) coupled with multi-angle laser-light scattering (MALLS) and refractive index (RI) detectors. The measurements were performed in duplicate.

2.2.2. M_W of the water-soluble fraction before and after de-esterification and solubility in water before de-esterification

The water solubility of the starch films before the addition of NaOH was determined according to Menzel et al. (2013). To detect changes in molecular weight in the starch films, i.e. cross-linking due to CA esterification, the M_W of the water-soluble sample fraction of the starch films, before and after subsequent de-esterification was determined, as described in Menzel et al. (2013), using the HPSEC-MALLS-RI system. The measurements were performed in duplicate.

2.3. Molecular weight distribution of amylose and amylopectin

The amylopectin and amylose distribution was determined according to Menzel et al. (2013). In brief, starch film samples were dissolved to a concentration of 5 mg/mL in 0.1 M NaOH to break CA ester-linkages and an aliquot was subsequently fractionated by size-exclusion chromatography on a Sepharose CL-2B column (GE-Healthcare, Uppsala, Sweden). The profile of the eluting fractions was determined using the phenol–sulfuric acid method (DuBois, Gilles, Hamilton, Rebers, & Smith, 1956) and iodine staining (Morrison & Laignelet, 1983). The measurements were performed in duplicate.

2.4. Degree of di-esterification according to complexometric titration of CA with copper (II)-sulfate

The concentration of CA di-ester was determined using the complexometric titration method (Graffman, Domels, & Strater, 1974; Klaushofer, Berghofer, & Steyrer, 1978) with the modifications described by Menzel et al. (2013). Based on the stable complex formation reaction of free and asymmetrically mono-esterified CA molecules with copper (II)-ions, two titrations were performed on the starch films. First, the film samples were hydrolyzed with 0.1 M KOH (pH > 12), adjusted to a pH of 8.5 with a borax/boric acid buffer and titrated with a 0.02 M copper (II)-sulfate solution. In a second titration, film samples were not hydrolyzed butonly pre-swollen in water, borax/boric acid buffer solution was added and the sample solution was titrated with the 0.02 M copper (II)-sulfate solution. The difference between the titrations of the hydrolyzed and non-hydrolyzed films enabled the degree of di-esterification to be calculated (Menzel et al., 2013). The measurements were performed in triplicate.

2.5. Gel content of cross-linked films

The gel content in formic acid was determined according to Reddy & Yang (2010) with small modifications described in Menzel et al. (2013). In brief, 0.1 g film sample was placed in 5 mL formic acid under mild stirring for both 24 h at 23 °C and 5 h at 50 °C. The

gel content was determined as the dry weight of the material that did not pass through a stainless steel mesh (Tyler mesh 30) and was expressed as percentage of dry film weight. The measurements were performed in triplicate.

2.6. Moisture content

The determination of the equilibrium moisture content for films stored at 23 °C and 50% RH is described in detail elsewhere (Olsson et al., 2013). The samples were equilibrated at 23 °C and 50% RH and the moisture content was determined gravimetrically after drying at 105 °C for 1 h. The measurements were performed in at least triplicate.

2.7. Moisture sorption

The method to determine the moisture sorption is described in more detail elsewhere (Olsson et al., 2013), however this time it was performed on film fragments instead of whole films. The measurements and equilibration was performed at 23 °C. Film fragments were first equilibrated at a low RH, below 25% RH, before being put into the controlled moisture generator where the measurements started at 50% RH. The weight was recorded as a function of time and RH. For the films which had not reached equilibrium at the end of each % RH stage, the equilibrium value was calculated assuming that the moisture uptake reached equilibrium asymptotically according to Olsson et al. (2013). After the trials, the dry weight of the films was determined gravimetrically by drying overnight at 105 °C and used to calculate the moisture content at the different RH. The measurements were performed in at least duplicate.

2.8. Thermal analysis

The effects of solution pH and curing temperature on the T_g of the starch films were determined by modulated differential scanning calorimetry, MDSC, using the method described in Menzel et al. (2013). In brief, a TA Systems DSC Q2000 (TA Instruments, New Castle, USA) was used and the scans were performed by heating the samples from 0 to 170 °C with an underlying heating rate of 2 K/min and a modulated heat amplitude of 0.318 K with a period of 60 s. The samples were equilibrated and sealed in hermetical cups at 23 °C and 50% RH. The inflection point in the reversible heat flow curve was taken as the T_g. All measurements were performed in at least triplicate.

2.9. Coat weight

The coat weight of the coated paper was measured gravimetrically as the difference in weight between coated and uncoated papers of the same area after conditioning at 23 °C and 50% RH for at least 24 h. The measurements were performed in triplicate.

2.10. Water vapor transmission rate

The water vapor transmission rate, WVTR, was measured with the gravimetric dish method, ISO 2528, using silica gel as desiccant. The test conditions were 23 °C and 50% RH and the results are presented in g/(m^2 24 h). The measurements were performed in triplicate.

2.11. Oxygen transmission rate

The oxygen transmission rate, OTR, was measured according to ASTM D3985-05 using a Mocon® OxTran® oxygen transmission rate tester, Model 2/21 (Mocon Inc., Minneapolis, MA, USA). The OTR measurements were performed at a constant temperature of 23 °C but using two different approaches to control the RH. In one approach the RH was kept constant at 50% RH during the entire experiment, while in the other approach equilibration and measurements were performed at 70% RH, directly followed by an increase to 80% RH (measurements were performed on the same films without removing from the machine). The measurements were performed in duplicate.

3. Results and discussion

3.1. Multi-angle laser-light scattering for the determination of weight-average molecular weight (M_W)

The results of the M_W determination are shown in Table 1. As reported in a previous study (Menzel et al., 2013), the M_W of the reference starch films without CA was about 9.0×10^6 to 9.9×10^6 g/mol for non-cured and cured films, respectively. Addition of 30 pph CA and curing at 150 °C severely degraded the starch, resulting in M_W of 0.2×10^6 g/mol. As expected, an increase in pH value of the starch solution resulted in higher M_W up to the M_W of the reference starch films without CA. As indicated by the results in Table 1, no significant starch degradation was observed at pH ≥ 4 and curing temperatures of 105 °C or lower. At the higher curing temperature (150 °C), however, pH ≥ 5 was required to prevent starch degradation. In a previous study (Menzel et al., 2013), it was shown that increasing CA content and curing the temperature resulted in reduction in M_W. This was explained in terms of more pronounced starch degradation at high CA levels and high temperatures due to acid hydrolysis of the glycosidic bonds in the starch molecules.

3.2. Molecular characterization of amylose and amylopectin

Changes in the amylose and amylopectin distribution can be detected by iodine staining and changes in the elution profile by size-exclusion chromatography, as reported by (Menzel et al., 2013), and are shown in the chromatograms in Fig. 2. There were two main peaks in the chromatogram, the first peak eluting between 55 and 70 mL corresponding mainly to amylopectin molecules with typically maximum absorbance, λ_{max} around 540 nm, and a broad second peak eluting between 80 and 150 mL corresponding mainly to amylose molecules and small amylopectin molecules with λ_{max} up to 610 nm (Morrison & Laignelet, 1983). At a lower solution pH and at higher curing temperature, the first eluting peak decreased due to acid hydrolysis of glycosidic bonds within the large amylopectin molecules. Amylose molecules,

Table 1
Weight-average molecular weight (M_W) of de-esterfied starch molecules in cured and non-cured starch films produced at different pH values of the starch-containing solution. Error limits indicate standard deviation based on duplicates.

Curing	M_W [10^6 g/mol] in NaOH				
	pH 2	pH 3	pH 4	pH 5	pH 6.5
Non-cured	6.1 ± 0.08	8.7 ± 1.18	9.2 ± 0.53	8.5 ± 1.12	9.7 ± 0.42
105 °C	5.8 ± 0.05	8.1 ± 0.76	9.1 ± 0.16	8.8 ± 1.15	9.4 ± 0.27
150 °C	0.2 ± 0.01	3.9 ± 0.14	4.8 ± 0.75	8.3 ± 0.93	9.5 ± 0.36

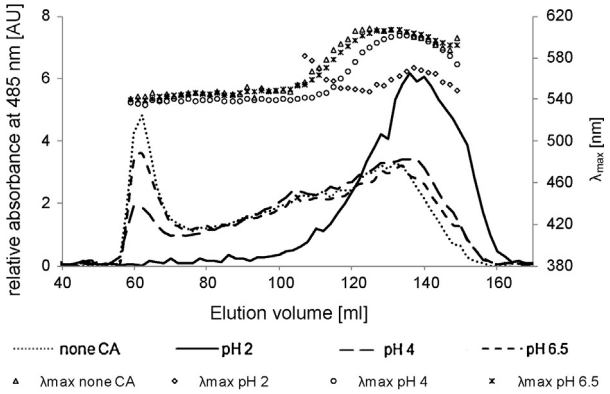

Fig. 2. Chromatograms (lines) and λ_{max} (dots) for starch films cured at 150 °C without CA and with 30 pph CA at pH 2, pH 4 and pH 6.5.

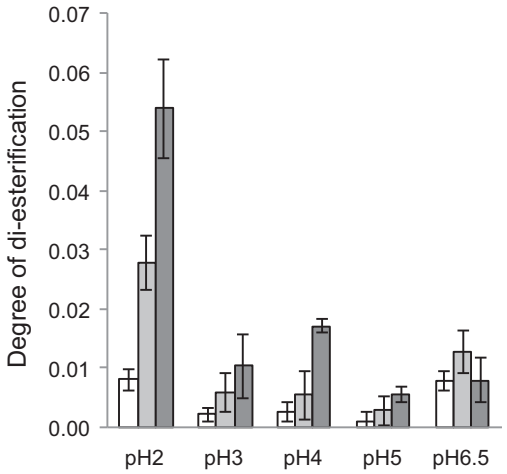

Fig. 3. Degree of di-esterification of starch films prepared at different pH values and curing temperatures, non-cured (white) and cured (105 °C – light gray and 150 °C – gray). Mean value of triplicates, error bars indicate standard deviation.

eluting later in the chromatogram, were probably also degraded, as seen by the decrease in absorbance in the elution interval 71 to ~120 ml as well by the decline in λ_{max} between 108 and 118 ml for the non pH adjusted starch film. However, the adjustment of the starch film formulation to a higher pH value reduced the starch degradation during film preparation, drying and curing. From the M_W measurements reported in Table 1 at pH ≥ 5, it was possible to cure films at 150 °C without any considerable degradation of starch. However, as seen in the chromatograms a low degree of degradation was detectable even at pH 6.5 (Fig. 2).

3.3. Degree of di-esterification according to complexometric titration of CA with copper (II)-sulfate

The amount of di-esterified CA ranged from 0.3 to 21% of total added CA (data not shown) and the corresponding degree of di-esterification (DDE) is given in Fig. 3. Films prepared at pH 2 showed the highest DDE values ranging from 0.008 to 0.054 indicating that in the latter case every 19th anhydroglucose monomer is di-esterified (data from Menzel et al., 2013). An increase in pH resulted in a lower di-ester content. For films with a pH between 2 and 5, an increase in curing temperature resulted in higher di-ester content (Fig. 3). At pH 6.5, no such trend was seen which can be a result of the low precision of the method.

The lower di-ester content at higher pH can be explained by the reaction mechanism for ester-bond formation (Fig. 1) since the reaction is catalyzed at low pH. The increase in di-ester content with higher temperature could be a result of the changed equilibrium due to residual moisture in the pre-dried starch films that evaporates during the curing at 150 °C, thereby increasing the yield of ester-bonds.

3.4. M_W of the water soluble-starch fraction before and after de-esterification and solubility in water

The M_W of the water soluble starch fraction before and after de-esterification was measured in order to detect cross-linkages between CA and starch molecules, as described in Menzel et al. (2013). The results of the M_W measurements are shown in Table 2 and water-solubility determinations are shown in Fig. 4. The M_W of the water-soluble fraction of the starch films showed that the starch films prepared at pH 2 and the films prepared at pH 3 and 4 and cured at 150 °C contained fractions with low M_W, which implies that the starch was severely hydrolyzed. This was not seen in the films prepared and cured at other solution pH levels and temperatures. A significant reduction in M_W after de-esterification of the water-soluble starch fraction was seen for the films prepared at solution pH ≤ 4 and in the films cured at 150 °C implying that cross-linking of starch by CA occurred at pH values between 2 and 6.5. One drawback of this analysis is that the cross-linking information is limited to the water-soluble part of the starch. The water-insoluble part of the starch film is expected to be even more cross-linked. However, the decrease in M_W after de-esterification indicated by this method showed that at least some of the di-esters shown in Fig. 3 are formed between two different starch molecules.

Table 2
Weight-average molecular weight (M_W) of water soluble starch films before (water) and after de-esterification (+ NaOH) and decrease of M_W after de-esterification of cured and non-cured starch films produced at different pH values of starch-containing solution. Error limits indicate standard deviation based on duplicates.

Curing	M_W [10^6 g/mol] and decrease in M_W after de-esterification				
	pH 2	pH 3	pH 4	pH 5	pH 6.5
Non-cured					
Water	0.41 ± 0.11	8.1 ± 1.81	9.5 ± 0.07	8.8 ± 0.54	10.3 ± 0.09
+ NaOH	0.33 ± 0.01	5.1 ± 1.26	8.7 ± 0.22	8.5 ± 0.63	10.1 ± 0.66
Decrease	19%	37%	8%	3%	2%
105 °C					
Water	0.27 ± 0.01	8.3 ± 1.15	9.6 ± 0.38	8.5 ± 1.10	10.8 ± 0.04
+ NaOH	0.22 ± 0.02	4.9 ± 0.7	8.5 ± 0.01	8.1 ± 0.81	10.1 ± 0.06
Decrease	18%	41%	11%	4%	6%
150 °C					
Water	0.34 ± 0.01	0.16 ± 0.01	0.19 ± 0.01	7.8 ± 0.95	10.2 ± 0.60
+ NaOH	0.051 ± 0.03	0.13 ± 0.01	0.15 ± 0.06	6.5 ± 0.55	9.5 ± 0.51
Decrease	85%	19%	21%	18%	7%

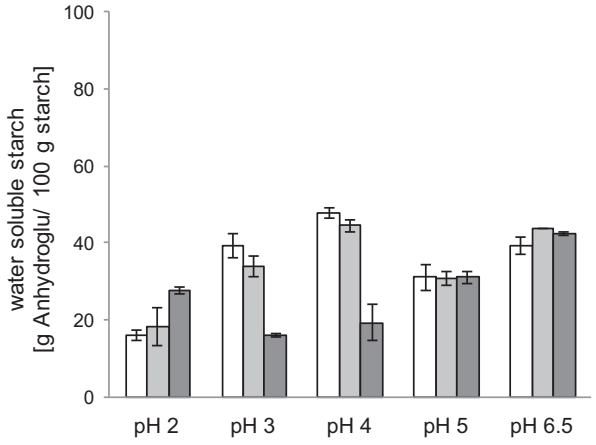

Fig. 4. Water-soluble starch content of starch films at different pH, non-cured (white) and cured (105 °C – light gray and 150 °C – gray). Mean value of duplicates, error bars indicate standard deviation.

The starch films prepared at pH 2 showed an increasing solubility in water with increasing curing temperature (Fig. 4), which was attributed to more extensive hydrolysis and hence more small starch molecules being dissolved (data from Menzel et al., 2013). In contrast, starch films with pH 3 and pH 4 showed a higher solubility in water when non-cured or cured at 150 °C than films prepared at pH 2, and the solubility decreased with increasing curing temperature probably due to higher cross-linking of starch. At pH 5 and 6.5, however, there were no significant changes in the water-solubility with temperature. Nevertheless, all CA-containing starch films showed a lower solubility in water than the reference starch films without CA (data not shown), which could be a result of the cross-linking of starch by CA. The complex interaction of the two concurrent reactions – hydrolysis and cross-linking – at different pH values resulted in the complicated water-solubility scatter.

3.5. Gel content in formic acid

The gel content corresponds to the fraction of the film that has a degree of cross-linking greater than the gel point, i.e. the amount of cross-linking needed for a partially cross-linked system not to be completely dissolved in a good solvent (Larson, 1999). The degree of cross-linking that is needed to reach the gel point is affected by the molecular weight. Hence, the measured gel content is affected by both hydrolysis and cross-linking.

The results of the gel content measurements are shown in Table 3. The non-pH-adjusted films (i.e. pH 2 in starch solution) have been described in detail elsewhere (Menzel et al., 2013). No starch gel was detectable neither in films prepared at pH 6.5 nor films cured below 150 °C prepared from pH-adjusted solutions. This demonstrated that in these starch films the degree of cross-linking was not sufficient to create a gel, whereas the conditions for preparation of starch films cured at 150 °C and adjusted to pH ≤ 5 and starch films at all curing temperatures prepared at pH 2 were sufficient to create a gel (Table 3). This is consistent with the data for the degree of di-esterification (Fig. 3) and water solubility (Fig. 4). At the highest curing temperature 150 °C, the gel content was higher and water solubility was lower at pH 3 and pH 4 than at pH 2 and 5. The difference in gel content might be due to less hydrolysis with increasing pH (Table 1), at the same time as cross-linking occured (Fig. 3).

For the films subjected to formic acid at 50 °C for 5 h (Table 3), i.e. more harsh conditions, it is evident that pH 3 and pH 4 resulted in the highest gel content. This measurement indicated that the predominant part of these films were strongly cross-linked, but without excessive hydrolysis of starch which would promote dissolution.

Table 4
Moisture content of films at 23 °C and 50% RH of starch films produced at different pH and different curing temperatures. Error limits indicate standard deviation based on at least triplicates.

Curing	Moisture content [%]				
	pH 2	pH 3	pH 4	pH 5	pH 6.5
Non-cured	8.0 ± 0.34	8.0 ± 0.59	7.3 ± 0.06	7.8 ± 0.04	11.2 ± 0.49
105 °C	7.6 ± 0.39	6.7 ± 0.71	6.9 ± 0.29	7.0 ± 0.48	11.1 ± 0.29
150 °C	8.6 ± 0.29	6.0 ± 0.90	4.9 ± 0.77	5.6 ± 0.43	11.2 ± 1.62

3.6. Moisture content

The equilibrium moisture content at 23 °C and 50% RH for the CA-containing starch films at different pH values is shown in Table 4, where it is obvious that a reduction in moisture content in the cured samples occurred when the pH of the starch–CA–water solutions was raised to pH 3, 4 and 5. For this, there are several possible explanations. It may be due to the reduction of hydrolysis (Table 1) with increasing pH although cross-linking still occurs (Fig. 3). In the case of the films adjusted to a pH between 3 and 5, there is a substantial reduction in the moisture content with increasing curing temperature. This can be explained by the increasing degree of di-esterification with increasing curing temperature (Fig. 3). At the same time, excessive hydrolysis is avoided, as seen in Table 1. Films with pH 6.5 showed much higher moisture content compared to films prepared at lower pH values. At pH 6.5, there were no changes in moisture content with increasing curing temperature, which may be due to the small differences in the degree of di-esterification (Fig. 4) and hydrolysis (Table 1) with increasing curing temperature.

3.7. Moisture sorption

The equilibrium moisture content at different RH levels for non-cured films with pH 2, 4 and 6.5 is shown in Fig. 5. Up to 60% RH, the films prepared at pH 4 had the lowest moisture content and the films prepared at pH 6.5 had the highest moisture content. At higher RH, however, the increase in moisture content was significantly larger for the films prepared at pH 4 compared to those at pH 2 or 6.5. The films adjusted to pH 6.5 showed an exceptionally small

Table 3
Gel content for CA-containing starch films produced at different curing temperatures and different pH values. Error limits indicate standard deviation based on triplicates.

Curing	Dissolving conditions	% Gel content in formic acid				
		pH 2	pH 3	pH 4	pH 5	pH 6.5
Non-cured	23 °C 24 h	4 ± 1	0	0	0	0
	50 °C 5 h	1 ± 1	0	0	0	0
105 °C	23 °C 24 h	75 ± 1	0	0	0	0
	50 °C 5 h	0	0	0	0	0
150 °C	23 °C 24 h	53 ± 6	80 ± 1	76 ± 5	4 ± 6	0
	50 °C 5 h	8 ± 6	64 ± 7	64 ± 12	0	0

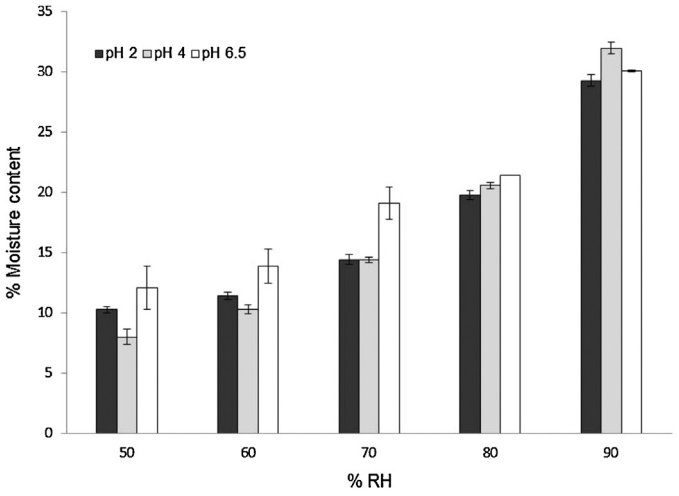

Fig. 5. Moisture content of non-cured films at different relative humidity. Error bars indicate standard deviation based on at least duplicates.

increase in moisture content between 70 and 80% RH, and the raw data, as exemplified in Fig. 6, showed that the films prepared from solutions adjusted to pH 6.5 exhibited a moisture uptake behavior different from what was expected, represented by the pH 4 sample. When the conditions changed from 70 to 80% RH, the films adjusted to pH 6.5 showed a rapid initial increase in moisture content and the moisture content then slowly dropped. This also occurred when the RH was changed from 80 to 90% even though the behavior was less pronounced.

This behavior, which at first glance seems quite unlikely, has been shown previously for both starch and gluten (Oliver & Meinders, 2011). However, the authors attributed this to an instability in the equipment at high RH levels and therefore did not further discuss their observations. However, it is clear from the data of Oliver and Meinders (2011), that this behavior started when the T_g of the starch and gluten films was the same as the experimental temperature for both starch and gluten. With increasing moisture content, the T_g of the films in the study by Oliver and Meinders (2011) dropped below the experiment temperature. This suggests that the behavior was not an artifact but was rather due to a change in the material properties, such as crystallization, occurring at or above T_g.

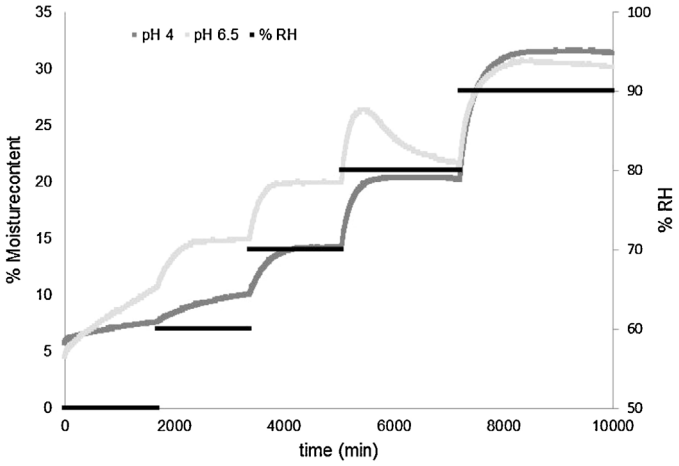

Fig. 6. Moisture uptake with time at different relative humidity for non-cured films with pH 4 and 6.5.

Table 5
T_g from MDSC for films produced at different pH and different curing temperatures. Error limits indicate standard deviation based on at least triplicates.

Curing	T_g [°C]				
	pH 2	pH 3	pH 4	pH 5	pH 6.5
Non-cured	58 ± 0.9	54.6 ± 0.7	56.6 ± 1.9	52.9 ± 3.1	63.9 ± 0.5
105 °C	59.6 ± 0.7	54.2 ± 1.2	55.3 ± 1.6	54.7 ± 3.0	65.5 ± 2.9
150 °C	57.5 ± 0.2	52.6 ± 1.0	53.1 ± 1.0	52.0 ± 2.0	64.8 ± 4.4

3.8. Thermal analysis

In a previous study, the addition of CA to starch was shown to reduce the T_g of starch films, especially at high CA content, but there were only rather small changes in the T_g between 20 and 30 pph CA (Menzel et al., 2013). It was also shown that at 20 pph CA or above, curing had no significant effect on T_g. That was attributed to the competitive reactions of hydrolysis and cross-linking and that mono-esterified CA can work as an internal plasticizer in the starch films (Menzel et al., 2013). The T_g of starch films containing 30 pph CA at different pH values and curing temperatures is shown in Table 5. There were clearly only minor differences in T_g between the different curing temperatures. Furthermore, there were only minor differences in the T_g at pH levels between 2 and 5, whereas the T_g increased significantly when the pH was raised to 6.5.

At first glance, these results seemed rather strange due to the differences in M_W (Table 1), cross-linking (Fig. 3) and moisture content (Table 4). For polymeric materials in general, T_g has been shown to increase with increasing molecular weight and crystallinity and to decrease with increasing degree of branching and flexibility of the chains (Bizot et al., 1997). However, cross-linking has been shown to only slightly affect the T_g of starch (Chang, Cheah, & Seow, 2000). Similar results were reported regarding the M_W (Bizot et al., 1997). In some reports, it has been shown that the T_g changes only slightly with moisture content when the amount of plasticizer is high, e.g. for glycerol (Chaudhary, Adhikari, & Kasapis, 2011; Forssell, Mikkilä, Moates, & Parker, 1997; Lourdin, Bizot, & Colonna, 1997), glycerol-diacetate (Lourdin, Coignard, et al., 1997), xylitol (Chaudhary et al., 2011) and for starch plasticized only by water (Chang et al., 2000; Perdomo et al., 2009).

The moisture content increased significantly when the pH was raised from 5 to 6.5, but despite this a significant increase in T_g was observed (Table 5). One reason could be different T_g values for the sodium salts of CA, which increase with increasing sodium content. T_g of CA is 11 °C and T_g of the sodium salts of CA are 69 °C, 115 °C and 158 °C for the mono-, di-, and tri-sodium citrate, respectively (Shalaev & Gatlin, 2010). However, the addition of salts to starch is very complex since it has also been reported to significantly reduce the T_g (Farahnaky, Farhat, Mitchell, & Hill, 2009).

3.9. Barrier properties of coated paper

The coat weight of double coated paper is given in Table 6, where it is clear that the coat weight depends on the drying temperature; the higher the drying temperature the lower the coat weight. One possible explanation of this is that a higher drying temperature did result in a smoother coating surface which was clearly seen by visual observation as the rod pattern was weaker with increasing drying temperature. A more even surface would lead to a slightly lower volumetric addition in the second coating. However, at least some of the decrease in coat weight seen with increasing drying temperature is probably also due to differences in moisture content of the coatings as seen in Table 4.

The WVTR at 23 °C and 50% RH according to the dry cup method is presented in Table 6. For comparison, the WVTR of the non-coated paper was roughly 200 g/(m^2 24 h). An increase in drying

Table 6
Coat wt, WVTR (dry cup) and OTR at different relative humidity for coatings with different pH and different drying temperatures. Error limits indicate standard deviation based on triplicates. For OTR, measurements performed in duplicate, both measurements are indicated.

Drying/property	Coat wt [g/m^2], WVTR [g/m^2 24 h] OTR [ml/m^2 24 h]				
	pH 2	pH 3	pH 4	pH 5	pH 6.5
70 °C					
Coat wt	18.1 ± 0.7	17.3 ± 0.1	16.1 ± 0.6	16.8 ± 1.2	18.5 ± 1.4
WVTR	28.7 ± 1.7	26.2 ± 1.2	25.5 ± 2.9	27.1 ± 0.5	41.4 ± 3.2
OTR 50	7/8		7/49		40/200
105 °C					
Coat wt	15.9 ± 0.7	15.5 ± 0.5	16.6 ± 1.1	16.4 ± 0.5	16.8 ± 0.8
WVTR	25.8 ± 2.0	22.5 ± 0.5	20.3 ± 2.1	20.3 ± 2.9	33.3 ± 1.8
OTR 50	3/6	5/8	5/35	6/140	3/100
OTR 70	12/13		7/9		560/880
OTR 80	56/60		48/51		500/690
150 °C					
Coat wt	14.80.28	14.7 ± 0.56	15.4 ± 0.8	15.0 ± 0.4	15.1 ± 0.1
WVTR	20.0 ± 0.9	17.9 ± 0.7	15.6 ± 1.7	17.6 ± 3.0	30.1 ± 0.6
OTR 50	3/7		3/6		2/6

temperature led to a lower WVTR for all the films at all the pH levels examined. One explanation, at least for pH levels between 3 and 5, is the reduction in moisture content in the free films (Table 4). Another explanation may be an increasing cross-linking of the material with increasing curing temperature, which is evident at all pH values except at pH 6.5 (Fig. 4) and which could reduce the starch chain mobility. At all curing temperatures, the WVTR reached a minimum at about pH 4. At pH 4, the cross-linking reaction, which would inhibit molecular movement, is still fairly efficient (Fig. 4), whereas the starch hydrolysis that would enable movement in the film was almost stopped (Table 1). The moisture content (Table 4) was also at a minimum at pH 4 for all curing temperatures.

Results of the OTR measurement at 50, 70 and 80% RH are given in Table 6. It was possible to produce coatings with fairly low OTR values at 50% RH (between 3 to 8 ml/(m^2 24 h)) at all pH values, even though there was a clear indication that the OTR values were higher for coatings produced at pH 6.5. For some experimental points, the difference between the duplicates was substantial, indicating that it was difficult to produce defect-free coatings. There was a weak trend toward lower OTR values at higher curing temperatures. It can nevertheless be concluded that an increase in curing temperature and low pH values did not increase the OTR. This is important since even though cross-linking in general reduces the mobility of the material, sometimes it can lead to increased permeability due to reduced density and increased free volume (Bresser, Boolchand, & Suranyi, 1986; Byun et al., 2007) which has been shown to strongly affect OTR (Byun et al., 2007).

When the OTR measurements were performed first at 70% RH, directly followed by measurements at 80% RH on the same sample (Table 6), there was a weak tendency toward lower OTR values at pH 4 compared to pH 2. One of the major aims of cross-linking is to render the films less water-sensitive at high RH. Fig. 4 shows that the cross-linking reaction takes place with less hydrolysis at pH 4 compared to pH 2. This combination of a relatively high degree of crosslinking and low degree of hydrolysis may be one explanation of the lower OTR values of coatings prepared at pH 4 compared to those prepared at pH 2. The OTR at 70 and 80% RH were significantly lower at pH 2 and pH 4 compared to pH 6.5. This is probably due to a low degree of cross-linking at pH 6.5 (Fig. 4). However, defects in these films could also result in high OTR values of the coatings produced at pH 6.5. For most water-sensitive barrier materials such as starch, it is normal that gas transport increases with increasing RH, as seen for starch coatings with pH 2 and pH 4. However, at pH 6.5 the OTR is reduced when the RH is increased from 70 to 80% RH. This behavior was extraordinary, but it coincided with the uncharacteristic moisture uptake seen in Fig. 6, and even though the moisture content increased slightly in the free films, the OTR of the coated paper decreased. This suggests that a structural change such as crystallization occured in the material. This is a phenomenon which could be of great interest for producing an oxygen barrier from starch that can be used at high relative humidity.

4. Conclusions

One major drawback of using CA as cross-linking agent and plasticizer in starch coatings for renewable barrier coatings in the packaging sector is the degradation of the starch material due to acid hydrolysis during industrial processing. This study shows that it is possible to produce coatings with improved barrier properties from starch cross-linked and plasticized with CA by adjusting the pH of the starch coating formulation. In order to prevent hydrolysis an adjustment to pH of 4 was shown to be sufficient. In addition, a minimum in WVTR was seen at pH 4, which was a reduction of more than 20% compared to non-adjusted starch coatings formulations (pH 2). At higher pH values, the WVTR increased and at pH 6.5, the WVTR was strongly elevated, compare to pH 2. Besides, fairly low OTR values at 50% RH (between 3 to 8 ml/(m^2 24 h)) for pH 4 coatings were achieved. This shows that it is possible to use starch with CA as a barrier material which has barrier properties comparable with today's petroleum based plastics.

As mentioned, two reactions were shown to affect the barrier properties of starch based coated paper during processing, hydrolysis and cross-linking. In this regard, several molecular techniques were used to show that the two concurrent reactions which affect the starch molecular weight in opposite directions, can be controlled by a suitable choice of pH and reaction temperature (curing). It was shown that the hydrolysis reaction was affected more strongly by an increase in pH than the cross-linking, being reduced more than the cross-linking reaction. Hydrolysis stopped almost completely at pH $\geq$ 4 at curing temperatures $\leq$ 105 °C and at pH $\geq$ 5 at curing temperatures $\leq$ 150 °C, whereas cross-linking still occurred to some extent even at pH values as high as 6.5 and at drying temperatures as low as 70 °C.

This study describes a possibility to produce renewable barrier coatings based on solutions of starch with a non-toxic cross-linker, citric acid, with minimized hydrolysis. The coatings are industrial applicable in a cost-efficient manner and are an alternative to petroleum based products.

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References

Andrews, B. A. K., & Reinhardt, R. M. (1996). Enhanced cotton textiles from utilization research. In Glenn Fuller, Thomas A. Mckeon, & Donald D. Bills (Eds.), *Agricultural materials as renewable resources* (pp. 32–45). Washington, DC: American Chemical Society.

Bizot, H., Le Bail, P., Leroux, B., Davy, J., Roger, P., & Buleon, A. (1997). Calorimetric evaluation of the glass transition in hydrated, linear and branched polyanhydroglucose compounds. *Carbohydrate Polymers*, *32*, 33–50.

Bresser, W., Boolchand, P., & Suranyi, P. (1986). Rigidity percolation and molecular clustering in network glasses. *Physical Review Letters*, *56*, 2493–2496.
Byun, Y. J., Hong, S. I., Kim, K. B., Jeon, D. H., Kim, J. M., Whiteside, W. S., et al. (2007). Physical and chemical properties of gamma-irradiated EVOH film. *Radiation Physics and Chemistry*, *76*, 974–981.
Campbell, A. M., & Briant, A. M. (1957). Wheat starch pastes and gels containing citric acid and sucrose. *Journal of Food Science*, *22*, 358–366.
Chang, Y. P., Cheah, P. B., & Seow, C. C. (2000). Plasticizing–antiplasticizing effects of water on physical properties of tapioca starch films in the glassy state. *Journal of Food Science*, *65*, 445–451.
Chaudhary, D. S., Adhikari, B. P., & Kasapis, S. (2011). Glass-transition behaviour of plasticized starch biopolymer system – a modified Gordon–Taylor approach. *Food Hydrocolloids*, *25*, 114–121.
Coma, V., Sebti, I., Pardon, P., Pichavant, F. H., & Deschamps, A. (2003). Film properties from crosslinking of cellulosic derivatives with a polyfunctional carboxylic acid. *Carbohydrate Polymers*, *51*, 265–271.
Dastidar, T. G., & Netravali, A. N. (2012). 'Green' crosslinking of native starches with malonic acid and their properties. *Carbohydrate Polymers*, *90*, 1620–1628.
DuBois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., & Smith, F. (1956). Colorimetric method for determination of sugars and related substances. *Analytical Chemistry*, *28*, 350–356.
Farahnaky, A., Farhat, I. A., Mitchell, J. R., & Hill, S. E. (2009). The effect of sodium chloride on the glass transition of potato and cassava starches at low moisture contents. *Food Hydrocolloids*, *23*, 1483–1487.
Forssell, P., Lahtinen, R., Lahelin, M., & Myllarinen, P. (2002). Oxygen permeability of amylose and amylopectin films. *Carbohydrate Polymers*, *47*, 125–129.
Forssell, P. M., Mikkilä, J. M., Moates, G. K., & Parker, R. (1997). Phase and glass transition behaviour of concentrated barley starch–glycerol–water mixtures, a model for thermoplastic starch. *Carbohydrate Polymers*, *34*, 275–282.
Gaspar, M., Benko, Z., Dogossy, G., Reczey, K., & Czigany, T. (2005). Reducing water absorption in compostable starch-based plastics. *Polymer Degradation and Stability*, *90*, 563–569.
Gaudin, S., Lourdin, D., Forssell, P. M., & Colonna, P. (2000). Antiplasticization and oxygen permeability of starch-sorbitol films. *Carbohydrate Polymers*, *43*, 33–37.
Ghanbarzadeh, B., Almasi, H., & Entezami, A. A. (2011). Improving the barrier and mechanical properties of corn starch-based edible films: Effect of citric acid and carboxymethyl cellulose. *Industrial Crops and Products*, *33*, 229–235.
Graffman, G., Domels, H., & Strater, M. (1974). Rapid determination of citrate in washing and cleansing agents by titration with Cu-solution. *Fette, Seifen, Anstrichmittel*, *76*, 218–220.
Habibi, Y., & Dufresne, A. (2008). Highly filled bionanocomposites from functionalized polysaccharide nanocrystals. *Biomacromolecules*, *9*, 1974–1980.
Hansuld, M. K., & Briant, A. M. (1954). The effect of citric acid of selected edible starches and flours. *Journal of Food Science*, *19*, 581–589.
Hirashima, M., Takahashi, R., & Nishinari, K. (2005). Effects of adding acids before and after gelatinization on the viscoelasticity of cornstarch pastes. *Food Hydrocolloids*, *19*, 909–914.
Huang, M., Yu, J., & Ma, X. (2006). High mechanical performance MMT-urea and formamide-plasticized thermoplastic cornstarch biodegradable nanocomposites. *Carbohydrate Polymers*, *63*, 393–399.
Jiugao, Y., Ning, W., & Xiaofei, M. (2005). The effects of citric acid on the properties of thermoplastic starch plasticized by glycerol. *Starch/Stärke*, *57*, 494–504.
Jonhed, A., Andersson, C., & Jarnstrom, L. (2008). Effects of film forming and hydrophobic properties of starches on surface sized packaging paper. *Packaging Technology and Science*, *21*, 123–135.
Klaushofer, H., Berghofer, E., & Steyrer, W. (1978). Starch citrates – production and technical application properties. *Stärke*, *30*, 47–51.
Larson, R. G. (1999). *The structure and rheology of complex fluids*. New York: Oxford University Press.
Lopez-Rubio, A., Lagaron, J. M., Ankerfors, M., Lindstrom, T., Nordqvist, D., Mattozzi, A., et al. (2007). Enhanced film forming and film properties of amylopectin using micro-fibrillated cellulose. *Carbohydrate Polymers*, *68*, 718–727.
Lourdin, D., Bizot, H., & Colonna, P. (1997). 'Antiplasticization' in starch – glycerol films? *Journal of Applied Polymer Science*, *63*, 1047–1053.
Lourdin, D., Coignard, L., Bizot, H., & Colonna, P. (1997). Influence of equilibrium relative humidity and plasticizer concentration on the water content and glass transition of starch materials. *Polymer*, *38*, 5401–5406.
Magalhães, N. F., & Andrade, C. T. (2009). Thermoplastic corn starch/clay hybrids: Effect of clay type and content on physical properties. *Carbohydrate Polymers*, *75*, 712–718.
Mathew, A. P., & Dufresne, A. (2002). Plasticized waxy maize starch: Effect of polyols and relative humidity on material properties. *Biomacromolecules*, *3*, 1101–1108.
Menzel, C., Olsson, E., Plivelic, T. S., Andersson, R., Johansson, C., Kuktaite, R., et al. (2013). Molecular structure of citric acid cross-linked starch films. *Carbohydrate Polymers*, *96*, 270–276.
Morrison, W. R., & Laignelet, B. (1983). An improved colorimetric procedure for determining apparent and total amylose in cereal and other starches. *Journal of Cereal Science*, *1*, 9–20.
Ning, W., Xingxiang, Z., Na, H., & Jianming, F. (2010). Effects of water on the properties of thermoplastic starch poly(lactic acid) blend containing citric acid. *Journal of Thermoplastic Composite Materials*, *23*, 19–34.
Olivato, J. B., Grossmann, M. V. E., Bilck, A. P., & Yamashita, F. (2012). Effect of organic acids as additives on the performance of thermoplastic starch/polyester blown films. *Carbohydrate Polymers*, *90*, 159–164.
Oliver, L., & Meinders, M. B. J. (2011). Dynamic water vapour sorption in gluten and starch films. *Journal of Cereal Science*, *54*, 409–416.
Olsson, E., Hedenqvist, M. S., Johansson, C., & Järnström, L. (2013). Influence of citric acid and curing on moisture sorption, diffusion and permeability of starch films. *Carbohydrate Polymers*, *94*, 765–772.
Perdomo, J., Cova, A., Sandoval, A. J., García, L., Laredo, E., & Müller, A. J. (2009). Glass transition temperatures and water sorption isotherms of cassava starch. *Carbohydrate Polymers*, *76*, 305–313.
Reddy, N., & Yang, Y. (2010). Citric acid cross-linking of starch films. *Food Chemistry*, *118*, 702–711.
Seidel, C., Kulicke, W., Hess, C., Hartmann, B., Lechner, M. D., & Lazik, W. (2001). Influence of the cross-linking agent on the gel structure of starch derivatives. *Starch/Stärke*, *53*, 305–310.
Shalaev, E. Y., & Gatlin, L. A. (2010). The impact of buffer on solid-state properties and stability of freeze-dried dosage forms. In F. Jameel, & S. Hershenson (Eds.), *Formulation and process development strategies for manufacturing biopharmaceuticals*. Hoboken, NJ, USA: John Wiley & Sons, Inc.
Shi, R., Bi, J., Zhang, Z., Zhu, A., Chen, D., Zhou, X., et al. (2008). The effect of citric acid on the structural properties and cytotoxicity of the polyvinyl alcohol/starch films when molding at high temperature. *Carbohydrate Polymers*, *74*, 763–770.
Shi, R., Zhang, Z., Liu, Q., Han, Y., Zhang, L., Chen, D., et al. (2007). Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melt blending. *Carbohydrate Polymers*, *69*, 748–755.
Svagan, A. J., Hedenqvist, M. S., & Berglund, L. (2009). Reduced water vapour sorption in cellulose nanocomposites with starch matrix. *Composites Science and Technology*, *69*, 500–506.
Wang, N., Yu, J., Chang, P. R., & Ma, X. (2007). Influence of citric acid on the properties of glycerol-plasticized dry starch (DTPS) and DTPS/poly(lactic acid) blends. *Starch/Stärke*, *59*, 409–417.
Wing, R. E. (1996). Starch citrate: Preparation and ion exchange properties. *Starch/Stärke*, *48*, 275–279.
Xie, X., & Liu, Q. (2004). Development and physicochemical characterization of new resistant citrate starch from different corn starches. *Starch/Stärke*, *56*, 364–370.
Yamada, T., Morimoto, Y., & Hisamatsu, M. (1986). Effect of citric acid on potato starch gelatinization. *Starch/Stärke*, *38*, 264–268.
Yang, C. Q., Xu, Y., & Wang, D. (1996). FT-IR spectroscopy study of the polycarboxylic acids used for paper wet strength improvement. *Industrial and Engineering Chemistry Research*, *35*, 4037–4042.
Yoon, S., Chough, S., & Park, H. (2006). Properties of starch-based blend films using citric acid as additive. II. *Journal of Applied Polymer Science*, *100*, 2554–2560.
Yu, J., Chang, P. R., & Ma, X. (2010). The preparation and properties of dialdehyde starch and thermoplastic dialdehyde starch. *Carbohydrate Polymers*, *79*, 296–300.