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Properties of Cast Films Made of HCl-Methanol Modified Corn Starch

The molecular and physicochemical properties of the studied starches modified with 0.36% HCl in methanol at 25 °C and 45 °C were related to the film properties of these starches. The weight-averaged molecular weight (M_w) and the number of long-chain branches (DP 13–36) of HCl-methanol modified starch decreased with increasing degree of acid modification, but the number of short-chain branches (DP < 6) increased. HCl-methanol modification significantly decreased the ghost formation in gelatinized starch dispersions and the viscosity of starch film-forming dispersions. Thus, the homogeneity of the produced starch films was improved and their opacity reduced. Proper HCl-methanol modification produced corn starch films with lower moisture absorption rate and maximum moisture content under high relative humidity (RH = 97%) condition.

Keywords: Corn starch; HCl-methanol modification; Cast film production; Molecular structure; X-ray diffraction pattern; Water vapor permeability

1 Introduction

Polymers obtained from renewable resources attracted more and more attention in recent years due to the increased price of crude oil, the policies for environmental protection, and the demands for safe and edible materials. These materials from renewable resources include carbohydrates, proteins, lipids, and microbial synthetic polymers from natural monomers and polymers. Starch, the dominant carbohydrate reserve material of higher plants, is an abundant and relatively inexpensive biopolymer. Starch-based films or coatings are effective gas barriers [1] and completely biodegradable materials in a wide variety of environments, and have the potential to replace synthetic polymers for manufacturing package materials in disposable food service items, containers, agricultural mulch films, and edible coatings or films [2, 3].

However, compared to plastics produced from fossil fuels these starch-based materials are very sensitive to moisture, and their structures and properties are easily changed with surrounding humidity. The molecular weights and structures, the ratio of crystalline to amorphous region, the polymer chain mobility, the plasticizers and the additives present are all important factors that influence the properties of starch films [4]. A strong film with high crystalline/amorphous ratio was obtained from

high-amylose starch, which resulted in low gas permeability [5]. Introducing synthetic polymers by grafting or copolymerizing with starches and adding acetic/fatty acid moieties into starch molecules through esterification significantly reduced the water absorption and water transmission of films [6, 7]. By cross-linking high amylose starch with epichlorohydrin, starch films showed brittle stress-strain behavior and high water vapor transmission rate (WVTR) [8]. Furthermore, films prepared with oxidized banana starch had higher water vapor permeability (WVP) and tensile strength than that prepared with unmodified starch [9].

Acid modification in aqueous dispersion has been used for decades in the starch industry to produce thin-boiling starches, but only a few studies about the film-forming properties of these starches have been made. A film with high tensile strength could be produced from intensively hydrolyzed barley starch ($M_w = 5 \times 10^5$), but no continuous films could be obtained from any of acid-modified potato starches [10]. Nevertheless, good qualities of cast films were formed by removing most of the sugars from the hydrolysates with dextrose equivalent (DE) 15–20 [11].

It is believed that glycosidic bonds in the amorphous regions are preferentially attacked by acids while limited conformational changes of crystalline starch are found due to the restriction of acid diffusion in this region [12, 13]. Acid-modified starches had higher degrees of crystallinity and lower amylose content than unmodified ones [14]. Small [15] reported that acid-modified starch prepared in 95% ethanol containing 0.2–1.6% HCl for 6–15

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min had a minimum amount of low molecular weight dextrin. The limit dextrin with a specific range of molecular weight could be controlled by performing the hydrolysis reactions in specific solvent systems and at specific reaction temperatures [16–18].

In this study, the molecular changes of HCl-methanol modified corn starch and the properties of film-forming dispersions were investigated using high-performance size-exclusion chromatography (HPSEC), high-performance anion-exchange chromatography (HPAEC), the Rapid Visco Analyser (RVA), and light microscopy. The findings are expected to provide an improved knowledge of the effect of HCl-methanol induced starch modifications on properties of starch cast films, and will be discussed in relation to moisture barrier properties of the films.

2 Materials and Methods

2.1 Materials

Native corn starch was purchased from Gu-Tong Foods Industrial Ltd. (Chia-Yi, Taiwan). HCl-methanol modified corn starch was prepared by treatment with 0.36% HCl in methanol at 25 °C and 45 °C for 6 h, 12 h, and 48 h [19]. Amylopectin was isolated and purified by fractional precipitation with ethanol [20, 21]. Isoamylase (EC 3.2.1.68) of *Pseudomonas amyloclavata* (59,000 U/mg) was purchased from Hayashibara Biochemical Laboratories, Inc. (Okayama, Japan). All reagents were analytical grade or higher and used as received.

2.2 Molecular structure of HCl-methanol modified corn starch

The molecular structures of starches were characterized with HPSEC and HPAEC according to systems described in our previous publication [22]. Starch (30 mg) was dissolved in 90% dimethyl sulfoxide (DMSO, 1 mL) with continuous stirring in a boiling water bath for 10 min then stirring at room temperature overnight. The starch dispersion was mixed with 0.1 M aqueous NaNO_3 of 70 °C containing 0.02% NaN_3 (30 mL) and filtered through a Nylon membrane filter (5.0 μm) (TITAN, NC, USA). The flow rate of the mobile phase was 0.7 mL/min. HPSEC determinations were performed in duplicate.

One milliliter of starch dispersion (30 mg/mL) was mixed with 6 mL of 70 °C H_2O and 6 mL of 40 mM acetate buffer (pH 3.5). After cooling to room temperature, 12 μL of isoamylase (5.9 U/ μL) was added to the starch dispersion and the mixture incubated at 37 °C in a water bath for 3 h. The debranched starch dispersion was filtered through a

poly(vinylidene fluoride) (PVDF) membrane filter (0.45 μm) and then injected into a HPAEC system. HPAEC determinations were repeated three times.

2.3 Starch cast film preparation

The film-forming dispersions were prepared using a Rapid Visco Analyser (model 4, Newport Scientific Pty, Ltd., Warriewood, Australia). The starch suspension (4.5%, w/w) with 1.2% glycerol was subjected to a temperature program of increasing temperature from 45 °C to 95 °C at a heating rate of 5 °C/min and then equilibrated at 95 °C for 10 min. Paddle speed was set at 125 rpm. 10 g of gelatinized starch dispersion was immediately poured into a Petri dish (i.d. 87 mm) and dried at room temperature and 50–60% relative humidity (RH) for 72 h. The starch films were used for the measurements of opacity, moisture sorption isotherms, moisture sorption kinetics and X-ray diffraction (XRD) and for light microscopical inspection. For the moisture vapor permeability experiment, the film-forming dispersion was prepared with the same formula and heating temperature program of RVA except the paddle speed was set at 960 rpm for the first 10 s and 160 rpm for the rest of time. The gelatinized starch film forming dispersion in a Petri dish was then dried at 40 °C for 5 h.

2.4 Film characterization

The starch film was equilibrated at 25 °C for 24 h above saturated $\text{Mg}(\text{NO}_3)_2$ solution (54% RH) in a sealed container. The film thickness was determined using a micrometer (Teclock, Nagano, Japan) at six random positions at each film and two films were measured for each test. The film opacity was measured spectrophotometrically (Pharma Spec UV-1700, Shimadzu, Kyoto, Japan) and defined as the area under the absorbance spectrum between 400 and 800 nm [23]. The film sample was cut into a rectangular piece (1 × 3 cm), fixed on the surface of a spectrophotometer cell and the absorbance spectrum recorded. The film opacity determinations were repeated three times.

2.5 Water vapor permeability

The water vapor permeability test was conducted using a modified ASTM E96-00 method [standard test method for water vapor transmission of materials]. The film sample (6.5 cm in diameter) was equilibrated at 25 °C and 54% RH for 24 h, and then placed between two copper rings on the top of a plastic cell (6 cm in diameter), containing 15 mL distilled and deionized water (100% RH). The test

cell was placed inside a chamber ($13.5 \times 12.2 \times 7.5 \text{ cm}^3$) containing 100 g silica gel at 25°C . Silicon vacuum grease (DOW Corning, USA) was used to prevent the leakage of moisture through seals. The test cell was weighed at time intervals of 3 h over 24 h. Water vapor transmission rate (WVTR) and water vapor permeability (WVP) were calculated as $\text{WVTR} = \Delta W / (\Delta t \times A)$ and $\text{WVP} = (\text{WVTR} \times L) / \Delta P$, respectively; where ΔW is the weight loss of the test cell, L is the film thickness, A is the exposed area (28.26 cm^2) and Δt is the time under the partial water vapor pressure gradient ($\Delta P = 2533 \text{ Pa}$). The plastic cell without any film covered was used as a reference. The WVP determinations were performed in duplicate.

2.6 Moisture sorption

For the determination of moisture sorption isotherms film samples of 2 cm in diameter were dried in a chamber containing P_2O_5 for 72 h before being equilibrated at different RH%. Different saturated salt solutions (LiCl , MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, NaCl , and K_2SO_4) were prepared in the individual sealed container to create the specific RH% (11, 33, 53, 75, and 97%) at 25°C . Each film was periodically weighted until the two consecutive weights were equal. The moisture content of film samples was calculated from the increase in mass of the dried sample after equilibration at a given RH condition. The moisture sorption determinations were at least done in duplicate.

For measurement of moisture sorption kinetics, corresponding film samples were dried in a chamber with P_2O_5 for 72 h and then equilibrated at 25°C above saturated K_2SO_4 solution (97% RH). Sample weights were recorded as a function of time. The Peleg model ($M(t) = M_0 + (t / (k_1 + k_2 t))$) was used to fit film moisture absorption data, where $M(t)$ is the moisture content after time (t), M_0 is the initial moisture content, k_1 is the Peleg rate constant related to the mass transfer and k_2 is the Peleg capacity constant related to the maximum water adsorption capacity [24].

2.7 X-ray diffraction

X-ray diffraction patterns were recorded using a Geigerflex powder diffractometer (Regaku, Japan) operating at 35 kV and 15 mA with nickel-filtered CuK_α radiation ($\lambda = 154.2 \text{ pm}$). Scattered radiation was detected in the angular range of $4\text{--}40^\circ$ (2θ) at a speed of $2^\circ/\text{min}$ with a step width of 0.1° . A starch film (2 cm in diameter) being equilibrated at 25°C and 54% RH for 168 h was fixed on a slide with Vaseline. Relative crystallinity of film was calculated as described by Rindlav et al. [25]. The XRD determinations were repeated three times.

2.8 Statistical analysis

The data was analyzed with SAS software (Version 8.2, SAS Institute, Inc., Cary, NC). One-way ANOVA and LSD (Least significant difference) were used to analyze the differences at 5% confidence level to compare means across the treatments.

3 Results and Discussion

3.1 Molecular characterization of HCl-methanol modified starch

Molecular size distributions of native and HCl-methanol modified corn starches analyzed with HPSEC are presented in Fig. 1 Fraction 1 (F1), eluted at lower elution volumes, corresponds to amylopectin of native corn starch or degraded amylopectin of HCl-methanol modified corn starches. Fraction 2 (F2), a lower molecular weight component, corresponds to amylose of native corn starch or degraded amylopectin and amylose of HCl-methanol modified corn starches. This is consistent with earlier findings [13]. In HCl-methanol treatment, the acid, which had been carried by methanol and diffused into the starch granules, attacked the oxygen atoms of the $\sim\alpha$ (1 $\rightarrow$ 4) or α -(1 $\rightarrow$ 6) glycosidic bonds, generating an unstable carbocationic intermediate which subsequently reacted with water originally located inside the starch granules [12]. The decreases of the normalized RI responses of F1 and the increases of that of F2 with

Fig. 1. HPSEC profiles of native corn starch and HCl-methanol modified corn starches which were modified with HCl-methanol at 25°C for 48 h (b) at 45°C for 6 h (c) and 12 h (d).

Tab. 1. Weight percentage (%) and weight-averaged molecular weight (M_w) of HPSEC fractions of HCl-methanol modified corn starches.

Treatment		F1		F2		F1 + F2
Temperature [°C]	Time [h]	[%]	$M_w (\times 10^6)$	[%]	$M_w (\times 10^6)$	$M_w (\times 10^6)$
Native		61.9 (1.5) ^a	831 (161)	38.1 (1.5)	6.91 (4.14)	520 (114)
25	48	37.5 (0.6)	224 (32)	62.5 (0.6)	5.15 (1.29)	87 (14)
45	6	21.2 (0.3)	– ^b	78.8 (0.3)	2.70 (0.64)	38 (15)
45	12	7.8 (0.2)	– ^b	92.2 (0.2)	2.13 (0.60)	16 (5)

^a Standard deviation.^b Undetermined because of relatively small F1 weight fraction.

increasing reaction temperature and time (Fig. 1) are attributed to the effects of elevation of reaction temperature and extension of reaction time. Both temperature and time effects facilitate the diffusion of acid into the corn starch granules and increase the reactivity of the glycosidic bond. The weight fractions of F1 and F2 of native corn starch modified with 0.36% HCl in methanol at 25 °C for 48 h decreased from 61.9% to 37.5% and increased from 38.1% to 62.5%, respectively (Tab. 1). The overestimate of the relative F2 fractions compared to the theoretical amylose content of corn starch might result from the inevitable degradation in sample preparation and the incomplete separation of the two fractions.

When native corn starch was modified at 45 °C for 6 h and 12 h, most of the amylopectin molecules were degraded so that their M_w shifted to the F2 fraction. Furthermore, the M_w of the starch sample (F1 + F2) calculated from the HPSEC profile showed that the M_w of native corn starch (5.2×10^8) decreased with ongoing acid hydrolysis. The degradation degree of HCl-methanol modified corn starch was the most intensive in the case of treatment at 45 °C for 12 h ($M_w = 1.6 \times 10^7$) and the least intensive at 25 °C for 48 h ($M_w = 8.7 \times 10^7$). Robyt et al. [18] reported that the DP value of potato starch hydrolyzed in methanol with 0.36% HCl at 45 °C for 12 h was ~ 900 . Lin et al. [26] reported that the M_w of maize starch modified with 0.36% HCl in methanol at 25 °C for 48 h was $\sim 2 \times 10^7$. Differences between our results and reported data can be attributed to the varieties and sources of starches, and the methodology of molecular weight determination.

The amylopectin microstructures of the native and HCl-methanol modified corn starches were characterized by the chain-length distribution of side chains in the mole-

cules (Fig. 2). According to the chain-length distribution of amylopectin from eleven plant sources, the basic categories of the chain lengths of A-, B₁-, B₂-, and B₃-chains are in the ranges of DP 6–12, 13–24, 25–36, and > 37 , respectively [27]. The pulsed amperometric detector (PAD) responses per molecule, which depended on the DP and the resolution of the chromatograms, declined above DP 37. Thus, the chain-length distribution in Fig. 2 was fractionated into DP < 6 , 6–12, 13–24, and 25–36. There were no chains with DP < 6 in native corn starch. The relative percentage of DP < 6 fraction significantly increased with ongoing starch hydrolysis (Fig. 2, see box for details). The relative percentages of DP 6–12 and DP 13–24 fractions of corn starch modified at 45 °C for 12 h were increased significantly when compared with those of native corn starch but were decreased in comparison with other HCl-modified corn starches (25°C/48h and 45°C/6h). In the DP 25–36 fraction, the relative percentage of corn starch gradually decreased with ongoing acid hydrolysis. The HCl-methanol modification of starch was influenced by its granular architecture and the loosely packaged amorphous regions were preferentially attacked and then degraded into short chains [22]. As the results of acid hydrolysis, the relative percentages of B chains (DP 13–24 and 25–36) of amylopectin, which are usually partially located in amorphous regions, were decreased, while the DP < 6 and DP 6–12 were increased. The chains of these fractions are usually regarded as side chains of amylopectin.

3.2 Properties of film-forming dispersion

When a starch suspension is heated under a constant rate of shearing, the rise in viscosity is attributed to the swell-

Fig. 2. Chain length distribution of amylopectin of native corn starch and HCl-methanol modified corn starches. The same letter above bars means no significant differences ($p < 0.05$) among samples.

ling of starch granules. The fully swollen starch granules were broken down during continuous heating and stirring; thus the viscosity of the starch slurry decreased sharply (Fig. 3a). The solubilized amylose molecules entangled each other and the granular remnants which might contain amylopectin molecules were trapped in the dispersed starch. The pasting temperature, peak viscosity and final viscosity of native corn starch were 86 °C, 335 mPa·s and 210 mPa·s, respectively. With corn starch modified at 25 °C for 48 h and at 45 °C for 6 h peak viscosity dropped down to 39 mPa·s and 28 mPa·s and the final viscosity of film-forming dispersion was close to 0 mPa·s. The more extensively hydrolyzed starch had the lower viscosity of the starch film-forming dispersion. Moreover, HCl-methanol modified starches showed a lower pasting temperature (~ 76 °C) than native corn starch (86 °C). In comparison to native corn starch the lower pasting temperature and paste viscosity of acid-treated starch might be attributed to the etched amorphous regions of starch granules that resulted from the decrease in granular integrity. The decrease in viscosity of the starch film-forming dispersion was also related to the reduced molecular weight of starch (Tab. 1). Figs. 3(b-d) show the light microscopic images of starch film-forming dispersions obtained right after the preparation from RVA. In Fig. 3b, the film-forming dispersion made of native corn starch consists of a discontinuous matrix with swollen starch granules, ghost remnants, and leached-out amylose and amylopectin. This indicates that the heating profile used in this experiment is not sufficient to completely rupture the native corn starch granules. However, the film-forming

dispersions made of HCl-methanol modified corn starches are nearly homogeneous and only a small amount of starch fragments are observed (Fig. 3c-d). The homogeneous film-forming dispersions indicate that the HCl-methanol modified corn starches are almost completely ruptured and fully gelatinized. The low hot-paste viscosity of film-forming dispersions made of acid-modified starches is related to the high ratio of continuous phase (aqueous dispersions of amylose and amylopectin) to discontinuous phase (swollen starch granules and granular fragments). The low hot-paste viscosity of the film-forming dispersion is beneficial for starch film processing and its properties.

3.3 Optical characteristics

Fig. 4 shows the opacity of native and HCl-methanol modified corn starch films. The lower opacity values of films made of acid-modified corn starches indicates that the transmission of light through those films is much better than through films made of native corn starch. The opacity of native corn starch film is 96 ± 19 AU nm. When HCl-methanol modified starch is used for film processing, the opacity of starch films decreases to 25 – 37 AU nm. This results from the reduction of starch fragments and air bubbles in the HCl-methanol modified starch films. The bubbles are formed due to the high stirring rate of RVA, which are used for starch gelatinization and it is extremely difficult to get rid of them in case of pastes with high viscosity made of native starch. Furthermore, the larger standard deviations of the opacity values reflect the complicated and inhomogeneous phases inside the

Fig. 3. Pasting property of starch film-forming dispersions prepared and monitored by using a RVA (a) and micrographs of film-forming dispersions: native corn starch (b), HCl-methanol modified corn starch at 25 °C for 48 h (c), and 45 °C for 6 h (d).

Fig. 4. Opacity of the starch films made of native corn starch, HCl-methanol corn starches, PE film, and Parafilm. 25C48h, 45C6h, and 45C12h represent the starch films made of corn starch modified with HCl-methanol at 25 °C for 48 h, at 45 °C for 6 h and 12 h.

native corn starch film (ghosts and bubbles). The opacity of films made of native corn starches is similar to Parafilm while the films made of acid modified corn starches (45 °C/6 h and 45 °C/12 h) have an opacity similar to PE films.

3.4 X-ray diffraction

Native corn starch and HCl-methanol modified corn starches exhibit the typical A-type X-ray diffraction pattern of cereal starch, with sharp peaks at $2\theta = 15^\circ$, 17° , 18° and

23° (Fig. 5). Several researchers have reported that the X-ray crystallinity of starches increased after acid treatment because the amorphous regions of the starch granules are preferentially attacked and the chain segments in acid-hydrolyzed starch rearrange during the hydrolysis [14, 28, 29]. However, the crystallinity of native corn starch and corn starch modified with 0.36% HCl-methanol solution at 45 °C for 12 h are not significantly different (Fig. 5). The X-ray diffraction spectra of films made of native corn starch and HCl-methanol modified corn starches display in contrast a B-type pattern, which is

Fig. 5. X-ray diffraction spectra of native corn starch, native potato starch, HCl-methanol modified corn starches, and starch films made of native corn starch and HCl-methanol modified corn starches.

characterized by peaks at $2\theta = 5.6^\circ$, $14\text{--}15^\circ$, 17° , 19° , 22° and 24° just like the characteristic peaks of native potato starch (Fig. 5). The A-type crystalline structure of native and HCl-methanol modified corn starches is obviously disrupted during gelatinization. The recrystallization of starch molecules during the drying process of film-making results in the B-type crystalline structure. Furthermore, the V_H -type diffraction pattern, recognized by the additional peak at 21.5° (2θ), is found in the films. The V_H -type crystalline structure is made responsible for single-helical structures formed of complexes between amylose and glycerol or native lipids [30]. The peak intensity ($2\theta = 21.5^\circ$) of starch films made of native corn starch is higher than that made of HCl-methanol modified corn starch. An explanation for the observed differences might come from the fact that native lipids have been extracted by methanol and, furthermore, the high concentration of amylose outside the granular fragments enhanced the formation of amylose-glycerol/lipid complexes in the native corn starch film (Fig. 5). The relative degree of B-type crystallinity of the native corn starch film and of films made of corn starches modified at 25°C for 48 h, 45°C for 6 h and 45°C for 12 h is calculated to come to 18.38 ± 0.93 , 20.25 ± 0.60 , 20.09 ± 0.66 , and $21.09 \pm 1.09\%$, respectively. The relative degree of B-type crystallinity of the native corn starch film is significantly ($p < 0.05$) lower than that for HCl-methanol modified starch films, whereas there are no significant differences among modified starch films. The degree of crys-

tallinity in a polymer sample is dependent on the mobility of the molecule chains during the crystallization process [5]. Following this conception, the HCl-methanol modification of starch reduces the amount of granular fragments and lowers the viscosity of a film-forming dispersion (Fig. 3) that facilitates the mobility and rearrangement of starch molecules. Thus, the development of B-type crystalline is much faster in a HCl-methanol modified starch films than that in a native corn starch film.

3.5 Water vapor permeability

The water vapor transmission rates ($WVTR$) of corn starch films ($\sim 6.8 \times 10^{-3} \text{ gm}^{-2}\text{s}^{-1}$) are nearly half that of the control (plastic cell without film on top, $14.5 \times 10^{-3} \text{ gm}^{-2}\text{s}^{-1}$) (Fig. 6). The rate of water vapor transport through a starch film is composed of the rates of adsorption, diffusion, and desorption, where the water molecules dissolve in one side of the film, move within the void space among polymer segments and then desorb from the polymer surface on the other side of the film [31]. Chemical structure, ratio of amylose to amylopectin, polymer packing, crystallinity, plasticizer, and environmental humidity are all factors related to the permeability of starch films. It is believed that the polymer segments in crystalline structures are more tightly packed and that the mobilities of polymer chains in amorphous regions are also constrained by the crystalline structures. Therefore, the increase of crystal-

Fig. 6. WVTR and WVP of starch films made of native corn starch and HCl-methanol corn starches. 25C48h, 45C6h, and 45C12h represent the starch films made of corn starches modified with HCl-methanol at 25 °C for 48 h, at 45 °C for 6 h and 12 h.

linity usually inhibits the water permeability of films. The *WVTR* of films show no significant differences in spite of the increase of relative B-type crystallinity ($\sim 2\%$) of HCl-methanol modified corn starch films (Fig. 6). An acceptable idea might be that the slight increase in crystalline structure is not able to retard the water transport through the hydrophilic starch matrix efficiently. Moreover, the crystalline structure of the swollen corn starch and starch fragments embedded in films made from native starch is eventually totally disrupted, because characteristic Maltese crosses are absent (data not shown).

Both *WVTR* and *WVP* are parameters used for the comparison of water barrier properties of films. In theory, *WVP* represents the intrinsic permeability of films and is not affected by the film thickness [32]. Fig. 6 shows that the *WVP* of native corn starch films is slightly higher than that of HCl-methanol modified corn starch films.

3.6 Moisture sorption isotherms

The moisture content of corn starch films increases slowly with increases in equilibrium relative humidity up to 67%, beyond that a steep rise in the moisture content of films is observed (Fig. 7). Below 75% RH, the moisture content of both, native corn starch and HCl-methanol modified corn starch films, is not significantly different (Fig. 7), indicating that the models of interaction of starch, water, and glycerol molecules seem to be similar. However, a further increase in environmental humidity will lead, in principle, to a complicated binding system in the films, where water and glycerol can be either associated to OH groups of starch components through multilayer bindings or they are present in form of free water and free glycerol [33].

Fig. 7. Moisture absorption isotherm curves of starch films made of native corn starch and HCl-methanol modified starches.

Applying this concept to native corn starch films or films made of HCl-methanol modified corn starch allowed to understand the differences in their moisture above 75% RH (Fig. 7). The higher moisture content of native corn starch films may be also attributed to the less homogeneous film structure together with a lower degree of crystallinity (see Fig. 3). The rougher surface of native corn starch films may also result in higher moisture contents due to an increased surface area and enhanced capillary effects.

3.7 Moisture sorption kinetics

The moisture contents of the native corn starch film and films produced from HCl-methanol modified corn starches reach 75 and 50–60 g water/100 g solids after 5 h (Fig. 8). When stored for 30 h the moisture content is 110 and 75–85 g water/100 g solids, respectively. All the starch films absorb moisture quickly at an early stage. During the following phase the moisture absorption rate becomes much lower. The moisture contents at different periods of time were fitted by using the Peleg model [24] and the respective parameters presented in Tab. 2. The calculated correlation coefficients ($r^2 > 0.95$) indicate that the Peleg equation allows a good fit to the experimental data. The initial moisture sorption rate is in the order native corn starch film $> 45^\circ\text{C}/12\text{h} > 25^\circ\text{C}/48\text{h} > 45^\circ\text{C}/6\text{h}$, since the lower k_1 represents the higher sorption rate [35]. The order of the magnitude of k_2 values is in agreement with those of k_1 . As k_2 is a constant related to the maximum water absorption capacity, a lower k_2 represents a higher absorption capacity of the film [34]. The large amount of water absorbed due to a higher absorption rate

Fig. 8. Moisture absorption of starch films made of native corn starch and HCl-methanol modified starches equilibrated at 97% relative humidity. The lines were derived from Peleg's equation.

Tab. 2. Peleg equation's parameters of native corn starch film and starch films made of HCl-methanol modified corn starches.

Treatment		k_1	k_2	r^2
Temperature [°C]	Time [h]	[h/(g water/g solids)]	[g solids/g water]	
Native		2.911	0.815	0.959
25	48	4.061	1.187	0.974
45	6	4.339	1.198	0.962
45	12	3.049	1.115	0.964

of the film made of native corn starch during storage is attributed to a disorder in the film matrix that is caused by swollen starch granules and granular fragments. Films made of acid-modified starch show a smaller moisture sorption rate and a reduction in the amount of absorbed water. However, films produced with too intensively modified starch ($45^\circ\text{C}/12\text{h}$) demonstrate again a higher absorption rate and also a higher water absorption capacity. This is attributed to a serious degradation of polymer chains, which become too short to provide sufficient intermolecular entanglement, which is necessary for good film formation.

4 Conclusions

Proper HCl-methanol modification of corn starch provides a good biopolymer resource for the starch film processing with improvements in the performances of opacity and moisture sorption behavior during storage. The moisture contents of films made of HCl-methanol modified corn starches significantly decrease compared with native corn starch film at $\text{RH} > 75\%$. The homogeneity of native starch film structure is disturbed by the starch ghost fragments, which are embedded in the film architecture. In contrast, the HCl-methanol modification decreases the pasting temperature and paste viscosity that facilitate the completion of starch gelatinization and is beneficial for film formation. Excess acid modification could dramatically degrade starch molecules and produce small molecular segments that result in insufficient chain entanglements in film-forming dispersions of starch. Thus, poor film properties are observed when extensively acid-modified starch is used for film-making. This study provides information that corn starch with proper acid-methanol modification has improved film-forming properties. Research is underway to investigate whether acid-modified starch in aqueous dispersion also can improve the film properties and how to incorporate nanoparticles into starch films and their influences on the properties of starch nanocomposite films.

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