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Carbohydrate Polymers 54 (2003) 1–11

Carbohydrate Polymers

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# Surface octanoylation of high-amylose potato starch films

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Received 31 July 2002; revised 10 March 2003; accepted 12 March 2003

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## Abstract

In this study high-amylose potato (HAP) starch films were prepared by casting from aqueous solution. The relative crystallinity of the HAP films was determined to be 25% using wide angle X-ray diffraction. The films were surface esterified with octanoyl chloride and pyridine using heterogeneous reaction conditions. The chemical composition and the degree of starch substitution of the films were determined with electron spectroscopy for chemical analysis. The esterification reaction at the surface was initially very fast. The HAP films had a degree of substitution of approximately 2 after only 15 min at 80 °C. Attenuated total reflectance FT/IR measurements of the films revealed that the depth at which the esterification took place was at least 1.1 μm. FT/IR transmission analysis through a tablet of the film showed that esterification was not taking place to a high degree in the bulk and was thus concentrated to the surface region. An experimental design was used to optimise the degree of starch substitution by varying concentration, temperature and time. The experiments showed that the degree of starch substitution could be varied from 0.24 to 2.79 depending on treatment conditions, where the concentration of octanoyl chloride was the most important parameter. The morphology of the modified HAP films, as shown by scanning electron microscopy, exhibited a rougher surface structure than the unmodified films. The surface energy of the modified HAP films (~40 mJ/m$^2$) was lower than for unmodified HAP films (~50 mJ/m$^2$), as determined by static contact angle measurements. Water vapour transmission and water absorption measurements revealed that the water penetration through the HAP films decreased almost linearly with the degree of starch substitution.

*Keywords:* Starch; High-amylose starch; Surface modification; Esterification; Chemical modification; Octanoyl chloride

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## 1. Introduction

The excessive amount of disposables used in modern society has led to serious demands for biodegradable plastic materials made from renewable sources. Starch is a biopolymer that is an attractive renewable alternative to fossil fuel for the production of plastic materials used in food packaging, hygienic products, and even as biomaterials. Starch is found in the majority of plants and is easily isolated at low cost. By various processing techniques, such as extrusion (vanSoest, Benes, dewit, & vliegenthart, 1996), compression moulding (Glenn & Orts, 2001), injection moulding (Stepto, 2000) and micro-wave techniques (Lewandowicz et al., 2000), starch can be made thermoplastic and thus be converted into a variety of polymeric products using conventional processing equipment. Starch has also been found to possess good film-forming properties (Rindlav, Hulleman, & Gatenholm, 1997; Tomka, 1991). The films exhibit good mechanical properties (Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998) and are excellent oxygen barriers (Forssell, Lahtinen, Lahelin, & Myllarinen, 2002; Rindlav-Westling et al., 1998). On the other hand, the water vapour permeability has been reported to be high (Rindlav-Westling et al., 1998), which is explained by the hydrophilic nature of starch. The attractive film properties are attributed mainly to amylose, the long and primarily linear polyglucan of the two that are present in starch, rather than the highly branched amylopectin (Rindlav-Westling et al., 1998; Wolff, Olds, & Hilbert, 1951). Hence, high-amylose starches are of great interest in the development of starch-based films.

The hydrophilic nature of starch poses problems for the practical use of starch-based materials, however, but can be partly overcome prior to or during processing or by introducing hydrophobic substituents into the starch polymers. Numerous studies have been done with blends of starch and synthetic plastics (Griffin, 1973; Kim & Pometto, 1994; Nie, Narayan, & Grulke, 1995; Otey, Westhoff,

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doi:10.1016/S0144-8617(03)00121-8

Kwolek, Mehltretter, & Rist, 1969; Vaidya & Bhattacharya, 1994; Willett, 1992; Yang, Bhattacharya, & Vaidya, 1996). However, because of the hydrophilic nature of starch, most of the blends have poor mechanical properties as a consequence of lack of compatibility and thus poor interfacial adhesion. When chemically modified starch is blended with synthetic polymers, the biodegradability is higher than that of pure synthetic polymers but is low compared to pure starch containing materials. Esterification with fatty acids and acetylation of biopolymers, such as starch (Aburto et al., 1999a; Aburto et al., 1999b; Aburto et al., 1997; Billmers & Tessler, 1996; Lewandowicz et al., 2000; Miladinov & Hanna, 2000) and cellulose (Rowell, Tillman, & Zhengtian, 1986), is a common method for decreasing the water sensitivity of these biopolymers. It was previously found that octanoated starch esters with a high degree of substitution were biodegradable (Bikiaris et al., 1998). In esterification, fatty acids or acetyl groups are substituted onto one to three of the free hydroxyl groups in the polymer, in various degrees of substitution, three being the highest possible substitution value. With an increasing degree of starch substitution and concomitant growing fatty acid/starch ratio, the water solubility of the products is strongly reduced and organic solvents are needed to process the modified starch. Aburto et al. (1999a) reported contact angles up to 132° in octadecanoated corn starch with a degree of substitution of 1.8. The hydrophobicity increased with an increasing degree of starch substitution as well as with an increasing chain length of the fatty acids.

Bruno et al. (1995) reported a regioselective, enzymatic method for acetylating amylose deposited as a thin film. The method made it possible to direct an acetate group exclusively to the hydroxyl group on carbon number 6 of the surface accessible amylose molecules of the film using an organic-soluble protease preparation. Our hypothesis is that chemical surface esterification of starch films should be rather easy, since it has been proven to be successful on bulk starch. The amounts of chemicals used in a surface esterification would be significantly lower than for an esterification of bulk starch prior to film production. An efficient process of surface modification of starch films could have significant application industrially.

The aim of this study was to optimise the surface esterification process of films made of high-amylose potato (HAP) starch. The optimal modification reaction and the economy of reagent use in the surface modification process would be of value for industrial application in the field of packaging etc.

## 2. Experimental

### 2.1. Materials

HAP starch isolated from transgenic potato was kindly provided by Lyckeby-Stärkelsen (Kristianstad, Sweden). The reactants used in the esterification reaction were pyridine (≥99%) purchased from Sigma-Aldrich (Stockholm, Sweden) and octanoyl chloride (99%) from Acros Organics (Geel, Belgium).

### 2.2. Film formation

Films were made by solution casting. A starch solution (3% w/w in distilled water) was slowly heated to 130 °C in a heating/stirring module (Pierce, Rockford, Il, USA) and stirred continuously for the duration of the 3-h heat treatment. Aliquots of the starch solution were taken out at different times during heating to study the granule gelatinisation in a light microscope. After cooling to just below 100 °C, the solution was poured onto polystyrene Petri dishes ($\varnothing = 8.5$ cm) and dried to films. The starch films thus produced were then dried at 45 °C for 24 h.

### 2.3. Wide angle X-ray diffraction

Wide angle X-ray diffractograms of the HAP films were recorded in the reflection geometry on a Siemens D5000 diffractometer using nickel-filtered Cu K$\alpha$ ($l = 0.154178$ nm) radiation. An antiscatter slit of 0.6 mm, a detector slit of 0.2 mm and a scintillation detector were used. Diffractograms were taken between 5 and 30° ($2\theta$) at a rate of 1° ($2\theta$) per minute and a step size of 0.1° ($2\theta$). The background was subtracted from the diffractogram by drawing a straight baseline at 7° ($2\theta$). The relative crystallinity was calculated by dividing the area of the peak at 15.6–18° ($2\theta$) by the total area (Hermans & Weidinger, 1948). The diffractograms were smoothed.

### 2.4. Electron spectroscopy for chemical analysis

Electron spectroscopy for chemical analysis (ESCA) was used to determine the chemical composition of the starch films. ESCA analysis was performed using a PHI Quantum 2000 Scanning ESCA Microprobe instrument (Physical Electronics, Ismaning, Germany). An Al peak of 1486.6 eV was used at 20 kW and 10 mA as an X-ray source. Multipak V6.0A from Physical Electronics was used to evaluate the results. Photo-emitted electrons were collected at take-off angles of 15, 45 and 75°, corresponding to an analytical depth of 2, 5 and 8 nm, respectively (Garbassi, Morra, & Occhiello, 1998).

### 2.5. Surface modification

The degree of starch substitution as a function of reaction time was studied in the octanoylation of HAP films. The starch films were cut into small pieces ($1 \times 3$ cm, $\sim 15$ mg) and dried at 45 °C for 24 h in a vacuum oven prior to esterification. Pyridine in a quantity of 8 ml was added to a vial and 0.2 ml of octanoyl chloride was then added drop-wise to the vial. The dried piece of starch film was added to the vial and the reaction mixture was heated in a Pierce heating/stirring module, pre-set to 80 °C. The samples were kept in the heating/stirring module for times ranging from 1 to 300 min. All the measuring points are the average of at least two different runs. After reaction, the starch films were washed three times with acetone and then dried in a vacuum oven for 24 h at 45 °C prior to analysis.

An experimental design was set up to investigate the influence of the three variables: time, temperature and concentration of octanoyl chloride on the degree of substitution at the surface of the HAP films. The design was a two level full factorial design with three variables ($2^3$). A statistical software program, Modde (Umetrics, Umeå, Sweden), was used to set up the experimental design. The program randomises the run order of the experiments and calculates the influence of each variable and possible interactions between the variables, using multiple linear regression.

### *2.6. ATR-FT/IR*

Attenuated total reflectance FT/IR spectra were measured (4000–750 $\mathrm{cm}^{-1}$) with a Perkin Elmer 2000 FT-IR (Shelton, CT, USA) using a germanium and a zinc-selenid crystal as the internal reflection element. A MCT (HgCdTe) detector was used and the sample chamber was purged with dry air. An average of 100 spectrums was used to increase the signal to noise ratio.

### *2.7. Transmission FT/IR*

Transmission FT/IR was measured (4000–750 $\mathrm{cm}^{-1}$) with a Perkin Elmer 1000 FT-IR (Shelton, CT, USA). A small piece of a starch film was grinded together with KBr (Fluka) and then pressed at 10 metric tons to form a tablet. The average of 50 spectra was used to increase the signal to noise ratio.

### *2.8. Scanning electron microscopy*

Scanning electron microscopy (SEM) was used to monitor the surface topography of the modified starch films. SEM analysis was done using Zeiss DSM 940A equipment (Göttingen, Germany). The samples were sputtered with a layer of gold with an Edwards sputter coater S150B (Cheshire, UK). The samples were fastened onto metallic sample holders with conducting silver glue.

### *2.9. Contact angle*

Contact angle measurements were made using a contact angle gonimeter model 100-00, Ramé-Hart Inc. (Mountain Lakes, NJ, USA). A 2-μl droplet of the two measuring liquids, ultra-filtrated deionised water and methylene iodide, was placed on the starch film surface with a syringe. The droplet was observed under a low magnification microscope, and the resulting contact angle was measured using a gonimeter that fit into the eyepiece. The contact angle of the droplet was measured after 1 min. The ambient air humidity was 31% and the temperature was 23 °C during the measurements.

### *2.10. Water absorption*

Water absorption was measured by using 16 × 10 mm film strips, 40 μm thick, according to the ASTM D570-98 standard. The measurements were made by soaking the samples in distilled water. At regular time intervals (24 h), each sample was removed from the water tank, carefully dried with a paper cloth and weighed in an analytical balance with a precision of 0.1 mg to determine water uptake. Water absorption was measured as long term immersion, the samples thus returned to the water after each measurement. Weighing was repeated until the increase in weight for three consecutive determinations averaged less than 1% since the last weighing.

### *2.11. Water vapour transmission*

Water vapour transmission (WVT) was measured at 54.4% relative humidity. The measurements were made by attaching the starch film over a vial containing a saturated aqueous salt solution of $Mg(NO_3)_2$. According to ASTM E104-85, the relative humidity over a saturated aqueous solution of $Mg(NO_3)_2$ at 20 °C corresponds to 54.4%. The samples were weighed in an analytical balance with a precision of 0.1 mg and then placed in a desiccator with a relative humidity of $<4\%$. At regular time intervals (24 h), the samples were removed from the desiccator and weighed in the analytical balance to determine weight loss. The WVT was calculated from the decrease in weight per time elapsed and area of the film and is presented in $\mathrm{g/m^2\,h}$.

## **3. Results and discussion**

### *3.1. Film formation*

HAP starch was dissolved by heating in excess water. The gelatinisation process was followed by light microscopy. Aliquots were removed from the starch solution during heating to study the disintegration of the granules as shown in Fig. 1. As can be seen in Fig. 1b, the granules were highly swollen but not fully disrupted at 100 °C. Fig. 1c shows a sample heated to 120 °C. First at this temperature, proof of disrupted starch granules can be seen in the left side of the micrograph granules can be seen in the left side of the micrograph. Complete disruption takes place at a temperature of 130 °C as can be seen in the lower left corner of Fig. 1d. The gelatinised starch solution was poured onto Petri dishes and allowed to dry in ambient temperature and humidity to form films. All films were coherent, smooth

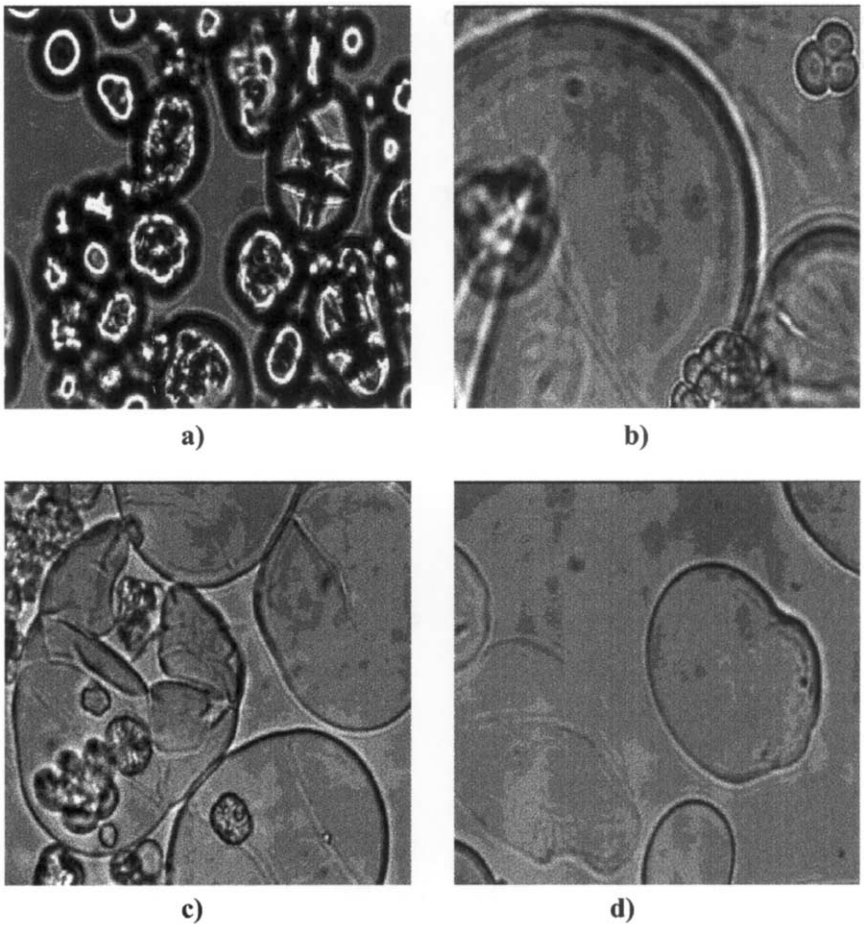

Fig. 1. Light microscope pictures of a 3% HAP aqueous solution at (a) RT (b) 100 °C (c) 120 °C (d) 130 °C.

and translucent. The relative crystallinity of the HAP films was determined by wide angle X-ray diffraction to be 25%. A relative crystallinity of 25% is higher than values reported for films of normal potato starch. Rindlav et al. (1997) determined the relative crystallinity to be 16% for a casted film of normal potato starch formed at 58% RH and 20 °C.

### *3.2. Surface modification*

High-amylose starch films were surface modified in a heterogeneous system using pyridine and octanoyl chloride. The mechanism of the reaction is shown in Fig. 2. In the first step, the free electron pair of nitrogen in pyridine performs a nucleophilic attack on the carbonyl carbon of octanoyl chloride. A complex is created with positively charged nitrogen and a negatively charged oxygen atom. The carbonyl group is subsequently regenerated during leaving of the chloride atom which is a relatively good leaving group. In the second step, an equivalent nucleophilic attack on the carbonyl carbon of the complex is performed by the free electron pair of oxygen (hydroxyl group) in starch. The carbonyl group is regenerated during the leaving of pyridine. Pyridine is a strong nucleophil and a good leaving group. The hydroxyl group is not such a strong nucleophil that it could perform a nucleophilic attack in step 1, where the chloride atom is just a relatively good leaving group. The chloride atom is a relatively good leaving group but a poor nucleophil. This is the reason why the reaction does not proceed backwards, i.e. a nucleophilic attack on the carbonyl group by a chloride ion. Pyridine acts both as catalyst and solvent. In addition to having a catalytic effect, pyridine minimizes starch deterioration during esterification because it neutralises the hydrogen chloride formed during the reaction.

The chemical composition of the surface of unmodified and modified starch films was determined with ESCA. The C1s peak for an unmodified HAP film was deconvoluted into three peaks, Fig. 3a, and energies distinctive for different carbon moieties (Beamson & Briggs, 1992) were referenced to the carbon–carbon bond (C–C) at 285.0 eV, carbon singly bonded to oxygen (–C–O) at 286.8 eV, and carbon bonded to two oxygen atoms (–O–C–O) at 288.0 eV. A nitrogen content of 5–6% (data not shown) was detected on the surface of the unmodified HAP film. The nitrogen is believed to originate from proteins present in the native starch, e.g. starch synthesising enzymes etc. (Rindlav-Westling & Gatenholm, 2003). The peak derived from the C–C bond corresponds to as much as 32% of all the carbon

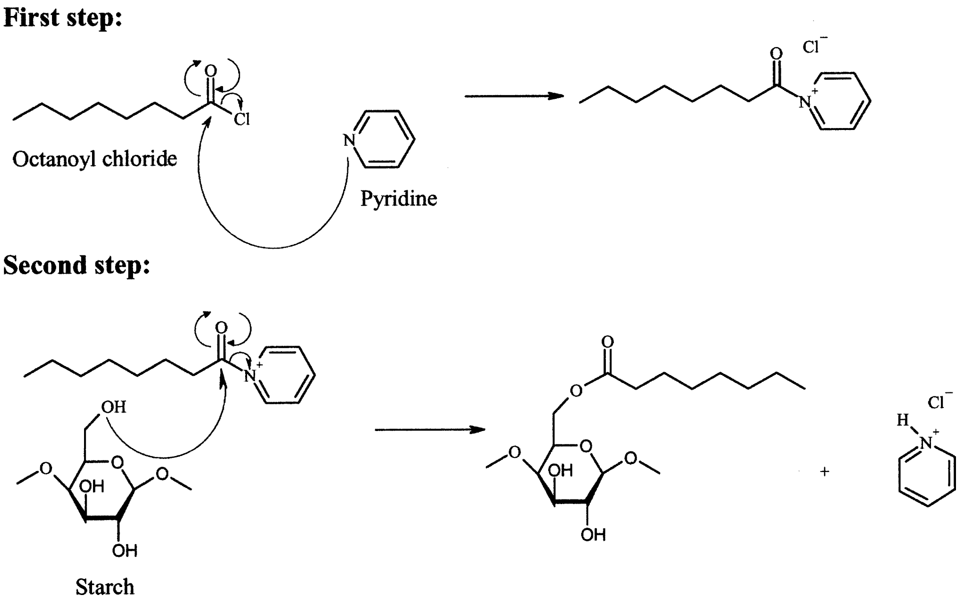

Fig. 2. General reaction mechanism of the esterification of starch. In the first step, pyridine performs a nucleophilic attack on the carbonyl carbon of octanoyl chloride and generates a complex. In the second step, the hydroxyl group of starch performs a nucleophilic attack on the carbonyl carbon of the complex resulting in octanoylation of starch.

present in the sample and is believed to originate from proteins, lipids and possible contaminations at the surface.

The C1s peak of a starch film that was treated for 1 h at 80 °C in a pyridine/octanoyl chloride solution is shown in Fig. 3b. The peak at 285 eV (C1), corresponding to C–C bonds in the hydrocarbon chain of octanoate, now dominates the spectrum. A new peak derived from the ester group (–O–C=O), C4 at 289 eV, is now also present in the ESCA spectra. The ester group is evidence of the esterification. The degree of substitution at the HAP film surface was determined as the ratio of the peak area of the (–O–C=O) peak at 289.0 eV that corresponds to ester and the peak area of the O–C–O peak at 288.0 eV in the glucose ring, C3. The degree of substitution of this sample was determined to be 1.8. The amount of nitrogen at the surface of the modified HAP films was very low ($<0.5\%$), indicating that the proteins present on the surface of unmodified starch film were dissolved from the surface by pyridine during the esterification reaction. The area ratio of 1:4.7–5.1 of O–C–O:C–O that was determined is close to the theoretical value of 1:5 for starch. Good agreement was also found for the area ratio of C–C:O–C=O (1:8). This indicates that the contribution of carbon bonded to nitrogen (–N–C=O) in proteins at about the same shift as carbon bonded to two oxygen atoms (288.0 eV) is not significant for the modified starch films.

### *3.3. Degree of starch substitution as a function of reaction time*

The degree of starch substitution as determined by ESCA as a function of reaction time was studied in HAP films in a solution of octanoyl chloride and pyridine at 80 °C, Fig. 4. The esterification reaction at the surface of the HAP films appeared initially to be very fast. During the first 15 min the degree of starch substitution increased linearly with reaction time to a degree of substitution of approximately 2. After this initial period of time the curve levelled off and reached a maximum degree of starch substitution of 2.5 after 2.5 h. The reproducibility of the method was investigated by treating five different HAP film samples with octanoylation solution for 15 min at 80 °C. ESCA analysis gave values of the degree of substitution varying between 1.8 and 2.1, indicating high reproducibility.

The degree of starch substitution shown in Fig. 4 corresponds to a sampling depth of approximately 5 nm. This sampling depth is obtained when there is a 45° angle between the sample and the electron detector in the ESCA analysis. There were no significant changes in the degree of starch substitution by collecting spectra at angle of 15 and 75°, which corresponds to sampling depths of 2 and 8 nm, respectively.

ATR-FT/IR measurements were performed on the films to determine the depth to which the esterification took place. A germanium and a zinc-selenid crystal were used as internal reflection element. The ester group absorbing at 1744 $\mathrm{cm}^{-1}$ was used as evidence of esterification. The depth of analysis at 1744 $\mathrm{cm}^{-1}$ was calculated according to Eq. (1):

$$d_\mathrm{p} = \frac{\lambda}{(2 \times \pi \times n_\mathrm{c}) \times \left( \sin^2 \theta - \left( \frac{n_\mathrm{s}}{n_\mathrm{c}} \right)^2 \right)^{1/2}} \qquad (1)$$

In Eq. (1), $d_\mathrm{p}$ is the depth of penetration, $\lambda$ is the wavelength, $n_\mathrm{c}$ is the refractive index of the crystal, $n_\mathrm{s}$ is

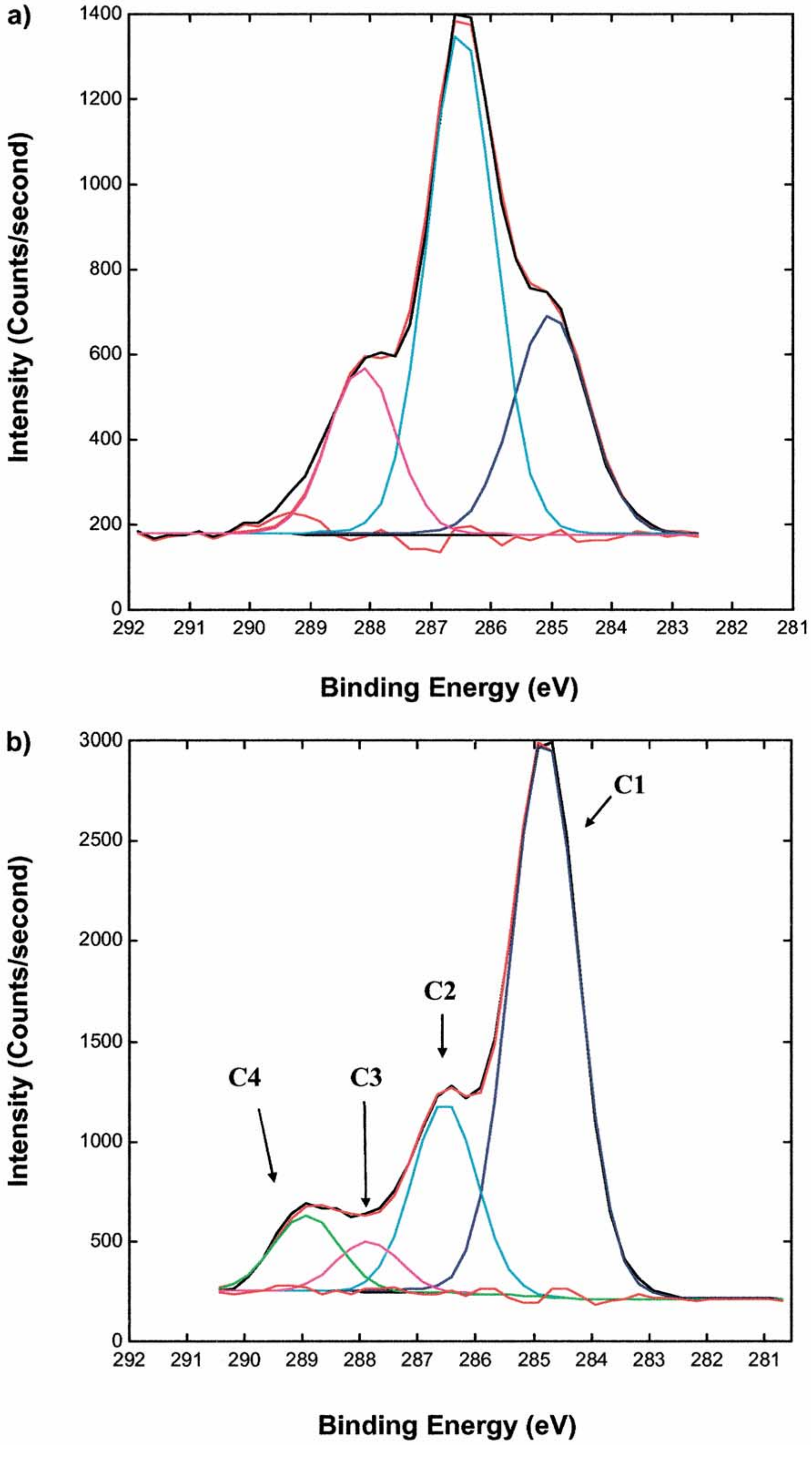

Fig. 3. Cls peak in the ESCA spectrum for (a) unmodified HAP film (b) A HAP film treated for 1 h at 80 °C in pyridine/octanoyl chloride solution with a determined degree of substition of 1.8. The depth of analysis was 5 nm in these experiments.

the refractive index of the sample and $\theta$ the angle of incidence. According to Eq. (1) the depth of analysis at 1744 $\mathrm{cm}^{-1}$ was 0.38 μm when the germanium crystal was used and 1.1 μm when the zinc-selenid crystal was used. As can be seen in Fig. 5 the ester group is still present at an analysing depth of 1.1 μm. This indicates that the esterification at least took place at a depth of 1.1 μm into the film. The degree of starch substitution of the film in the analyses was

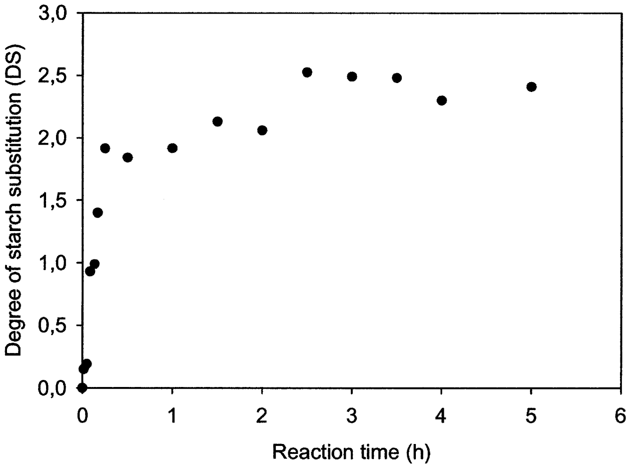

Fig. 4. Degree of substitution at the HAP film surface as a function of reaction time at 80 °C.

2.57. In addition, FT-IR transmission analysis through a tablet of the film mixed with KBr powder was also performed. As can be seen in Fig. 5 the absorbance at 1744 cm$^{-1}$ was significantly reduced. A broad band around 3400 cm$^{-1}$ from unsubstituted hydroxyl groups of starch is also present in this spectrum. This is evidence that the esterification was not taking place to a high degree in the bulk of the film and was thus concentrated to the surface region.

After esterification, the HAP films could easily be transferred from the vial without falling apart. A film of normal potato starch treated under the same reaction conditions was very swollen and softened and had a tendency to fall into smaller pieces. The reason for a greater mechanical stability in the HAP films as compared to normal potato starch films could be related to crystallinity. A higher degree of crystallinity counteracts solvent penetration into the material, thus swelling the structure.

### 3.4. Optimisation with experimental design

A two-level full factorial design with three variables ($2^3$) was set up to investigate the effect of treatment conditions and to be able to optimise the degree of substitution at the HAP film surfaces. The variables chosen were treatment time, which varied between 15 and 300 min, treatment temperature, which varied between 40 and 80 °C, and the concentration of octanoyl chloride, which varied between 0.036 and 0.28 M. The design also included three centre points. Table 1 summarises the experimental conditions used for treating each sample and the degree of starch substitution obtained by ESCA analysis. The degree of starch substitution varied between 0.24 and 2.79 depending on treatment conditions. Evaluation of the responses using linear regression with least square fit was used to model the process. Fig. 6 shows the calculated coefficients of the least squares model fitted to the experimental data. The concentration of octanoyl chloride was found to be an important parameter for maximising the degree of substitution at the HAP film surface, while time was of minor and temperature was of no importance in the studied interval. Some of the second grade terms (interaction terms) of the polynomial fitted to the experimental data were of significance. Negative values were found for the second grade terms of the concentration of octanoyl chloride and treatment temperature and a positive contribution was found

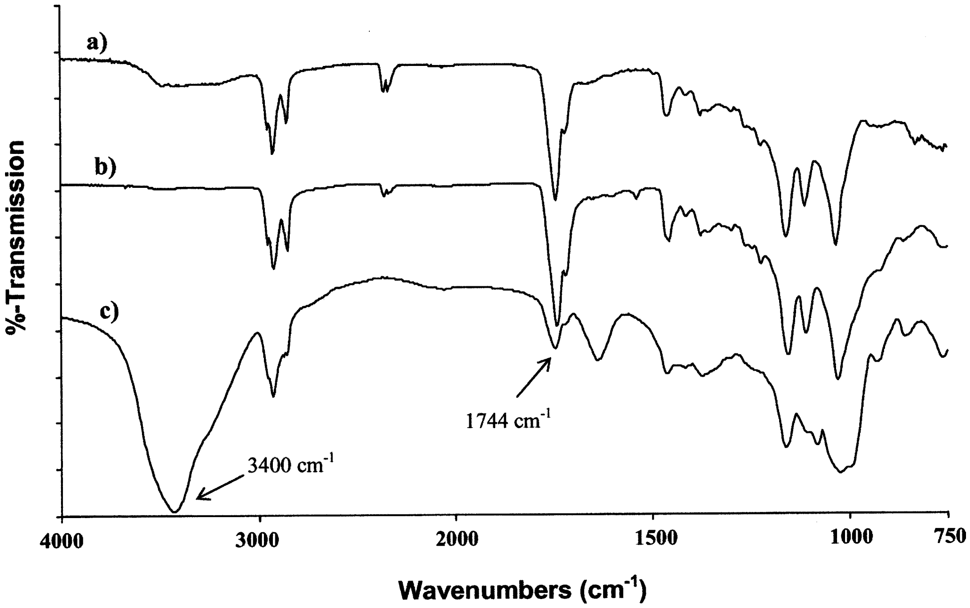

Fig. 5. (a) ATR-FT/IR (germanium crystal) (b) ATR/FT/IR (zinc-selenid crystal) (c) FT/IR transmission. The analyses were performed on a HAP film with a degree of substitution of 2.57. The depth of analysis at 1744 cm$^{-1}$ in the ATR-FT/IR measurements was 0.38 μm when a germanium crystal was used and 1.1 μm when a zinc-selenid crystal was used as an internal reflection element.

Table 1
Experimental conditions and resulting degree of substitution at the surface of the HAP films

| Sample | Time (min) | Temp. (°C) | Conc. (M) | Ds[a] |
|---|---|---|---|---|
| 1 | 15 | 40 | 0.036 | 0.31 |
| 2 | 15 | 40 | 0.280 | 2.57 |
| 3 | 300 | 40 | 0.036 | 0.28 |
| 4 | 300 | 40 | 0.280 | 2.38 |
| 5 | 15 | 80 | 0.036 | 0.24 |
| 6 | 15 | 80 | 0.280 | 1.77 |
| 7 | 300 | 80 | 0.036 | 0.35 |
| 8 | 300 | 80 | 0.280 | 2.79 |
| 9 | 157.5 | 60 | 0.036 | 0.91 |
| 10 | 157.5 | 60 | 0.280 | 2.77 |
| 11 | 15 | 60 | 0.158 | 2.00 |
| 12 | 300 | 60 | 0.158 | 2.28 |
| 13 | 157.5 | 40 | 0.158 | 1.92 |
| 14 | 157.5 | 80 | 0.158 | 2.11 |
| 15 | 157.5 | 60 | 0.158 | 1.89 |
| 16 | 157.5 | 60 | 0.158 | 1.96 |
| 17 | 157.5 | 60 | 0.158 | 2.61 |

[a] Degree of starch substitution.

for the interaction term between time and temperature. The contour plot in Fig. 7 shows the degree of starch substitution as a function of the concentration of octanoyl chloride and treatment time at a constant temperature of 80 °C. A high degree of substitution was found for high concentrations of octanoyl chloride and long reaction times.

### 3.5. Scanning electron microscopy

The surface morphology of the HAP films was investigated using SEM. Surface roughness of starch films have been shown in earlier studies (Rindlav-Westling et al., 2003) and explained as bulk phenomena, i.e. underlying structures in the bulk that affect the surface topography. The study stated that the roughness of the surface originated from a phase separation of amylose and amylopectin and the crystallinity of the bulk (Rindlav-Westling et.al., 2003). There was an obvious difference in the surface morphology of the modified HAP films and the unmodified films (not manipulated at all), as shown in Fig. 8. The unmodified HAP films showed no specific structure in the SEM micrograph and the surface appeared very smooth, as can be seen in Fig. 8a. Fig. 8b shows a micrograph of a HAP film that has been treated at 80 °C for 2 h in a solution of pyridine and octanoyl chloride. The surface of this film is rougher and more wrinkled. A first thought was that the surface roughness originated by dissolution of octanoylated starch and subsequent etching of the surface. However, a HAP film treated at 80 °C for 5 h in a solution of pyridine without an addition of octanoyl chloride appeared as rough as those to which octanoyl chloride had been added. The rough appearance of HAP films exposed to the modification process thus indicates that it is due to swelling and subsequent drying. This indicates heterogeneity of the HAP films which can origin from physical processes such as crystallization. The relative crystallinity of the HAP films was determined by wide angle X-ray diffraction to be 25%, which is higher than values reported for films of normal potato starch. A re-crystallization of crystals that melt at 80 °C when cooled to ambient temperature could thus affect the surface topography.

### 3.6. Surface energy

Contact angle measurements on unmodified (not manipulated at all) and modified HAP films were made for both ultra-filtrated deionised water and methylene iodide. At least three different measurements were made at each surface and the contact angle was measured after 1 min. The surface energy of the HAP films was calculated from the contact angle measurements using Wu's harmonic

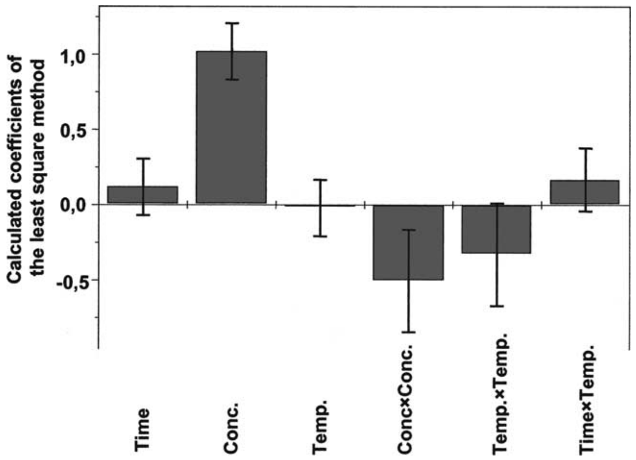

Fig. 6. Calculated coefficients of the least squares model fitted to the experimental data. Confidence intervals 95%.

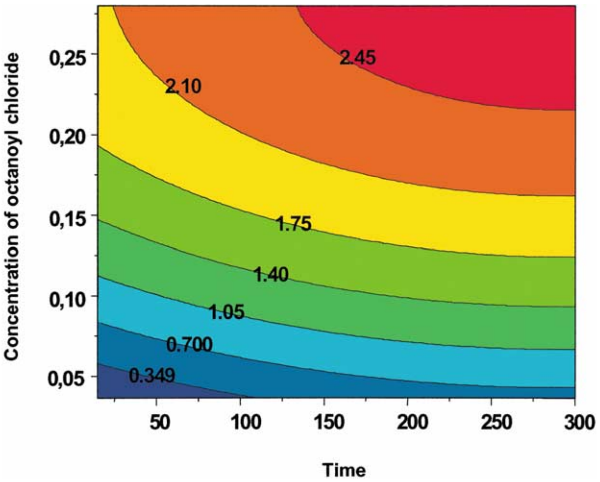

Fig. 7. A contour plot showing the degree of starch substitution as a function of concentration of octanoyl chloride and treatment time at a constant temperature of 80 °C.

mean method (Garbassi et al., 1998). A surface energy of ~ 50 mJ/m$^2$ was calculated from the contact angle measurements for unmodified HAP films. The surface energy of octanoylated HAP films treated for 1, 3 and 5 h reaction time was significantly lower than that of the unmodified films. An almost constant surface energy (~ 40 mJ/m$^2$) was found for the films treated for 1, 3 and 5 h, despite the fact that the degree of substitution at the surface of the HAP films varied between 1.9 and 2.5. However, several parameters that may influence the static contact angle measurements have not been studied here and deserve further attention, e.g. surface roughness, penetration of liquid, swelling and possible reorientation of surface molecules.

### 3.7. Water absorption

Water absorption was measured by soaking strips of HAP films in distilled water according to the ASTM D570-98 method. HAP films with different degrees of substitution were immersed in distilled water. The samples were soaked until the increase in weight per three consecutive weightings averaged less than 1% since the last weighting. There was a good correlation between the degree of starch substitution and the water absorption/resistance. The unmodified HAP film (not manipulated at all) absorbed the largest amount of water, with a 63% increase in weight compared to 42% for a HAP film with a degree of substitution of 2.11. A significant decrease in water absorption was observed when the degree of starch substitution was increased from 0.24 (59% increase in weight) to 1.77 (45% increase in weight). A higher degree of substitution than 1.77 seems to be of minor importance in reducing the water absorption. After the last weighing, the films were reconditioned at 50 °C for 24 h to determine possible dissolution of water-soluble materials. The amount of soluble materials was largest for the unmodified HAP film and decreased almost linearly with increasing degree of substitution. This correlates very well with the results of the ESCA analysis, which indicated that small amounts of proteins, peptides or contaminants at the surface were removed during modification. Longer reaction times during modification generated a higher degree of starch substitution and more efficiently removed the non-starch components from the HAP surfaces.

### 3.8. Water vapour transmission

WVT rate was measured at 54.4% relative humidity. WVT through the films appeared to be dependent on the degree of substitution at the HAP film surfaces. The WVT rate was highest through an unmodified film (13.9 g/m$^2$ h) and a film with a degree of starch substitution of 0.24 (14.1 g/m$^2$ h). Higher degree of starch substitution decreased the WVT rate through the films significantly. The WVT rate through films with a degree of starch substitution of 1.92 and 2.38 was measured to 9.3 and 7.8 g/m$^2$ h, respectively. The WVT rate seems to be almost constant with time for the duration of the 500 h-long experiment. Deviations from the trend lines were noted for

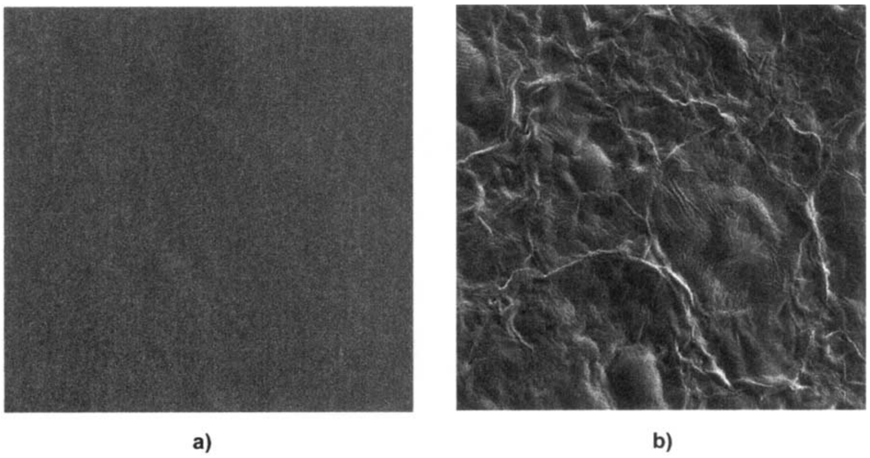

Fig. 8. SEM images of (a) Unmodified HAP film (b) HAP film treated for 2 h at 80 °C in octanoyl chloride/pyridine solution. Magnification x200.

all sets of data and were probably caused by an external influence, for example an increase in ambient temperature. The temperature was measured for the duration of the experiment and varied between 19 and 22 °C. A decrease in WVT rate to a constant level in the initial part of the experiment for all series was also observed. This could be explained as the time that elapsed before the dried films reach a saturation moisture content.

## 4. Conclusions

HAP starch films were prepared by casting from aqueous solution. Wide angle X-ray diffraction measurements showed that the crystallinity of the casted films was higher than previously reported for films of normal potato starch. The films were surface esterified with octanoyl chloride and pyridine using heterogeneous reaction conditions. The chemical composition and the degree of substitution were determined using ESCA. HAP films with a high degree of substitution at the surface were achieved after short reaction times. After only 15 min reaction in a solution of pyridine and octanoyl chloride the degree of substitution was approximately 2. ATR-FT/IR measurements revealed that the esterification at least took place at a depth of 1.1 μm into the films. Transmission FT/IR analysis showed that the esterification was not taking place to a high degree in the bulk of the film and was thus concentrated to the surface region. It was concluded from the experimental design for the parameters of treatment time and temperature and concentration of octanoyl chloride that the amount of octanoyl chloride was an important parameter in maximising the degree of substitution, while treatment time was of minor and temperature of no importance in the studied interval. The surface topography of the unmodified films appeared smooth without any specific structure, while the modified films had a significantly rougher surface structure, determined by SEM. The rougher surface of the modified HAP films is believed to be initiated by a phase-separation or re-crystallization in the bulk that affects the surface topography. Contact angle measurements showed that the surface energy was lower in the treated HAP films ($\sim 40$ mJ/m$^2$) than the unmodified HAP films ($\sim 50$ mJ/m$^2$). Water absorption and water transmission experiments revealed that the modified HAP films with a degree of substitution $>1.8$ were more resistant to water than unmodified HAP films.

## Acknowledgements

Lyckeby Stärkelsen is gratefully acknowledged for supplying HAP starch and for permission to publish this article. Vinnova is gratefully acknowledged for their financial support. Thanks to Martin Gustavsson, Anne Wendel, Anders Mårtensson and Max Östensson for their help with experiments and ESCA, SEM and ATR-FT/IR measurements.

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