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RESEARCH ARTICLE

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A green/sustainable organocatalytic pathway for the preparation of esterified supercritical CO_2-dried potato starch products

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Abstract

Production of renewable and modified starch-based products was achieved using a sustainable catalyst and an environmentally friendly drying process via supercritical CO_2. Potato starch was modified via a sustainable and green esterification process with acetic anhydride reagent implementing a novel organocatalytic pathway at different periods of time (0.5, 3 and 7 h) by applying an esterification reaction at 120°C targeting intermediate degrees of substitution (i.e., 0.2 < DS <1.5) finding potential applications as polymer packaging materials. The final modified samples were divided into two fractions, where the first fraction was dried under vacuum at 80° C for 24 h and the second fraction was dried under supercritical CO_2 at 40° C and 100 bars for 2 h. The final products were analyzed using an array of characterization techniques such as Fourier transform infrared (FTIR), Proton nuclear magnetic resonance (^{1}H-NMR), scanning electron microscopy (SEM), X-ray diffraction (XRD), N_2 physisorption, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and Karl Fischer. The chemical structure of both fractions was similar as confirmed by the different characterization techniques. Drying under supercritical CO_2 preserved some pores in the modified starch materials as opposed to thermal oven drying, as was confirmed by N_2 physisorption measurements. The degree of substitution (DS) was determined using three different techniques; titration, high performance liquid chromatography (HPLC) and solution state proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and the values were greater than 0.2 and less than 1.5 indicating intermediate degrees of substitution.

KEYWORDS

esterification, green, intermediate degrees of substitution, organocatalytic pathway, packaging, potato starch, supercritical CO_2, sustainable products

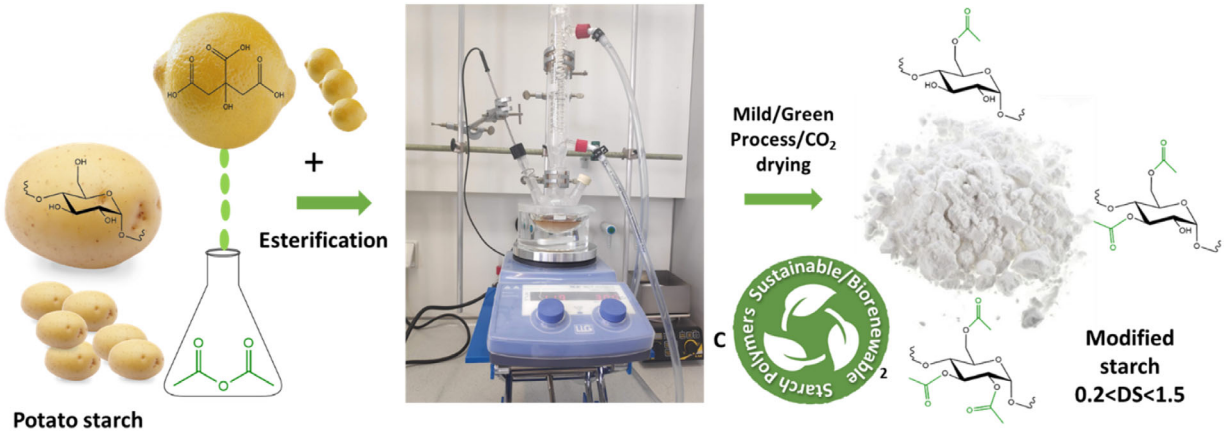
1 | INTRODUCTION

There is growing global impetus for a transition away from fossil fuel-based materials to enhance sustainable development, protect ecosystems, and reach net-zero targets. Synthetically derived, non-renewable polymers such as polyethylene, polypropylene, and polyvinyl chloride are particularly problematic due to their poor biodegradability,[1] and carbon-intensive production methods. Biomaterials such as starch are essential for the transition towards sustainably produced polymer products. Starch is a highly abundant,[2,3] renewable and biodegradable polymer. It is the primary energy storage in all green plants, and can be found in staple crops such as corn, potatoes, wheat and rice.[2,4] Its low cost, versatility and bio-compatibility makes it an ideal material to replace petroleum-based products.[5,6]

Industrially, starch is an important raw material used in a wide range of industries ranging from food and packaging to pharmaceuticals and biofuels.[5,7] According to Copeland et al.,[7] 60 million tonnes of starch are extracted annually, of which 60% is used in the food industry—either as a food product or additive (e.g., thickener, gelling-agent, stabilizer, preservation agent, or quality enhancer). The remaining 40% is used for pharmaceuticals (tissue and drug carriers), cosmetics, fertilizers, coatings, packaging, textiles, bioplastics, building materials and oil drilling (as an additive).[7] Most starches used in industry are modified to improve structural properties and functionalization.[4] Unmodified starch has the tendency to adsorb water at higher temperatures (typically insolubility in cold water) leading to expansion and eventually swelling of the crystalline region which disrupts the formation of hydrophobic colloids (gelatinization).[1] After cooling, the molecules of starch reorganize and restructure leading to an increase in viscosity and gel-like structure (retrogradation).[8] Amylose in particular has a greater tendency to retrograde, resulting in the formation of hard gels and strong films as opposed to soft gels and weak films produced by amylopectin.[9] Raw starches also tend to have unfavorable properties required for product development; with poor processability, low shear stress resistance,[3] poor cohesive qualities when heated up, and unwanted gel-like properties when cooled.[4] Reiterating, the hydrophilic nature of starch introduces the problem that comes along with the commercial use of native starch in industry, as the product is unstable and difficult to process.[10,11] Instability of the product during storage is mainly caused by starch being sensitive to moisture which affects its average molar mass due to hydrolytic degradation. Instability of the product in processing is mainly caused by unstable rheological properties of the starch as it is subjected to low pH, both high and low temperatures and shear forces due to mixing and pumping.[10] These disadvantages interfere with the application of starch as, for example, a biodegradable polymer that can be used in packaging materials. Due to its abundance and low cost, starch could play a key role in reducing the environmental footprint caused by fossil fuel based plastics. To omit the disadvantages of native starch and to create a more or less biodegradable material, starch has been used as a filler in petrochemical based materials.[12,13] Despite the composite structure, the hydrophilic character of native starch still raises serious concerns. This is attributed to the fact that petrochemical based plastics are rather hydrophobic, resulting in few favorable interactions that are created in the composite. Additionally, starch can be removed from the composite by microorganisms, decreasing the mechanical strength of the final product and increasing permeability.[14]

To overcome all of the aforementioned challenges, most starches used in industry are modified to improve structural properties and functionalization.[4] Modification can be achieved via chemical, physical, enzymatic or genetic engineering.[3,4,7,9,15] Chemical modification can involve esterification, etherification, cross-linking or starch-grafting whilst physical modification involves the use of heat, moisture or decomposition via hydrolysis or oxidation.[4] The purpose of modification is to enhance properties of starch that are imperfect for material manufacture. This includes increasing water solubility; decreasing the tendency to retrograde and form unstable gels; enhance texture, adhesion, and heat tolerance. Fortunately, chemical modification offers a pathway to overcome undesired properties of native starch. Depending on the final application of the starch product, a modification procedure can be chosen, in which the reagent, substrate, catalyst and method all influence the final properties of the product. Esterification is among the common processes used to modify starch. The conventional way of manufacturing these esterified starches is by treating the substrate (a certain starch) with a reagent (often an acid or anhydride) and a catalyst. Frequently, an alkaline catalyst in an aqueous medium such as sodium hydroxide is used.[14,16,17] Besides sodium hydroxide, pyridine can function as a catalyst. However, due to its high cost and toxicity, pyridine is not interesting for industrial use.[17] Motivated by environmental concerns, research in starch esterification has nowadays shifted towards the development of an environmentally friendly organocatalytic route to modify starch.[18,19]

The current study focuses on the esterification of potato starch using a sustainable and an efficient/non-pore destructive drying process. Potato starch is the starch of choice because of its abundance in the world and especially in the Netherlands. On a European scale,



SCHEME 1 Schematic representation of the organocatalytic pathway for potato starch esterification coupled with supercritical CO_2 drying. Intermediate degrees of substitution (0.2 < DS < 1.5) [Color figure can be viewed at wileyonlinelibrary.com]

52 million tonnes of potatoes were produced in 2018, in which the Netherlands ranks fourth in potato production, behind Poland, France and Germany. Hence, the main objective of this work is to explore the suitability of the organocatalytic method in the esterification of potato starch, as it proves to be a novel, sustainable way of modification. The method is sustainable, as depicted in Scheme 1. Indeed, supercritical CO_2 has an advantage in drying as it is sustainable, has a high diffusion coefficient and is expected to preserve the pores of the final modified starch material while maintaining a higher surface area of the final product as opposed to thermal drying, as will be shown in the results and discussion section. On the other side, vacuum oven drying leads to high surface tension (between the pore wall and solvent), leading to high capillary forces which is expected to collapse the majority of the pores of the material and this could alter the final material properties.

2 | EXPERIMENTAL PART

2.1 | Materials

Native potato starch (type B) (CAS: 9005-25-8) with a moisture content of 14.7% and an amylose content of about 25% was obtained from Sigma-Aldrich, and used without further purification. Acetic anhydride (≥99%, CAS: 108–24-7) and citric acid (CAS: 77-92-9) were both supplied from Sigma-Aldrich. Hydrochloric acid (30%, CAS: 7647-01-0) and sodium hydroxide (CAS: 1310-73-2) were laboratory grade chemicals purchased from Boom and Acros, respectively. Ethyl alcohol (96%, CAS: 64-17-5) and phenolphthalein (in ethanol 48%, CAS: 77-09-8) were purchased from Boom and used as received. Deuterated DMSO-d_6 (CAS: 2206-27-1) was supplied from Sigma-Aldrich for ^{1}H NMR analysis.

2.2 | Acetylation of potato starch via organocatalytic route

A 100 ml three-neck round-bottom flask was dried in the oven at 100°C. 25 ml acetic anhydride, 25 mmol citric acid and 2 g of native potato starch were added to the round-bottom flask as illustrated in Scheme 1. The flask was equipped with a magnetic stirrer and a reflux condenser to prevent the loss of acetic anhydride. As soon as the mixture reached a stable temperature of 120°C, the reaction was considered to be started. Esterification was run at three different reaction times: 0.5, 3, and 7 h. At the end of each reaction, the mixture was allowed to cool down to room temperature to avoid gelatinization upon washing. When the mixture reached room temperature, the solid product was separated from the liquid by means of vacuum filtration in a Buchner funnel with a 0.2 μm polyethersulfone (PES) membrane filter. The recovered solid was washed several times with distilled water. All experiments were repeated three times to ensure reproducibility. The final products were dried by two techniques: the first technique was carried out in a vacuum oven at 80° C for 24 h, while the other technique used supercritical CO_2 as a green, and efficient drying fluid at 40° C and 100 bars for 2 h. The chemical structure of all modified starch fractions using the two different drying techniques were the same as confirmed by an array of characterization methods.

2.3 | Determination of the degree of substitution (DS)

To determine the degree of substitution (DS), the titration method described by Tupa et al. was used.[11] About 200 mg of esterified sample were suspended in distilled

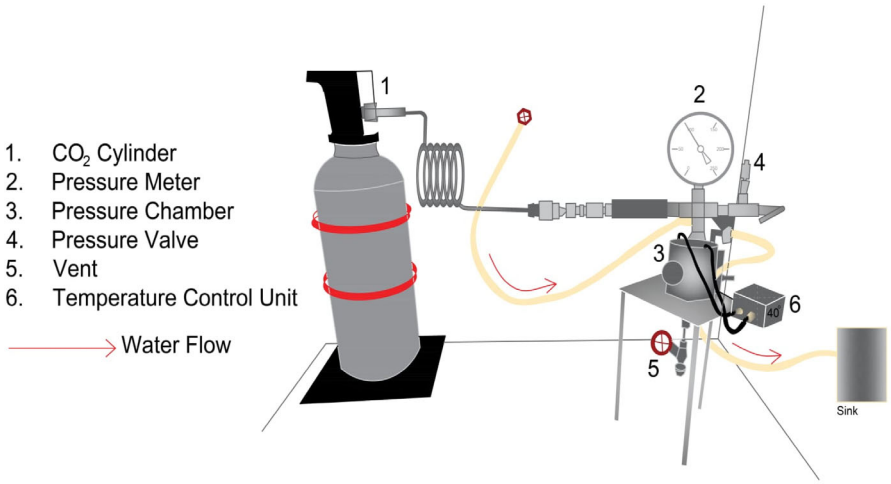


FIGURE 1 Supercritical CO_2 drying setup for modified starch products [Color figure can be viewed at wileyonlinelibrary.com]

water and sonicated for 10 min at room temperature to promote the separation of acetic anhydride and organocatalyst residues from the starch esters. All samples were washed thoroughly until the pH of the filtrate was about 7. Afterwards, samples were dried under supercritical CO_2 in a Stainless Steel Parr reactor, as shown in Figure 1, to ensure a negligible moisture content for calculating DS. This was corroborated with a Karl Fischer titration (KFT), see section 2.4.6. Samples were ground and about 100 mg were transferred to 100 ml Erlenmeyer flasks. A 75% ethanol solution was prepared and 20 ml were added to each Erlenmeyer flask. The flasks were heated to 50°C for 30 min. Subsequently, 20 ml of 0.1 M NaOH were added to each flask, using phenolphthalein as a basic indicator, and the flasks were once again heated to 50°C for 15 min. Afterwards, the flasks were stored at room temperature. Finally, the excess NaOH present in the flasks was back titrated with 0.1 M HCl using phenolphtalein as end point indicator. Besides the modified starches, also a blank sample (native potato starch) was taken through the whole procedure as a control sample.

The acyl content (%) was calculated using the following formula[11]:

$$Acyl\,(\%) = \frac{(V_B - V_S) * M_{HCl} * 10^{-3} * 100}{W},$$

where, V_B is the volume of HCl solution needed to titrate the blank solution, V_S the volume necessary to titrate the corresponding sample, M_{HCl} the concentration of HCl solution and W is the mass of the sample (g). The DS of all esterified starch samples was calculated by[11]:

$$DS = \frac{162 * Acyl\,(\%)}{43 * 100 - ((43-1) * Acyl\,(\%))},$$

where, 162 is the molar mass of the anhydroglucose unit and 43 is the molecular weight of the acetyl group of acetic anhydride.

2.4 | Characterization of starch esters

2.4.1 | Fourier-transform infrared spectroscopy (FTIR)

Infrared absorption spectra were recorded for the unmodified and esterified starch samples by FTIR in the attenuated total reflectance (ATR) mode, using a Shimadzu IRTracer 100 apparatus. Spectra were recorded taking scans in the wavelength range of 4000–600 cm^{-1} with 4 cm^{-1} resolutions. Esterified starches were purified by sonication and dried in the same manner as described in section 2.3 prior to FTIR measurement.

2.4.2 | Thermogravimetric analysis (TGA)

2–5 mg dried samples (50°C in vacuum for 7 h) were placed in a sample pan and heated from 30 to 750°C at a rate of 10°C min^{-1} in nitrogen atmosphere using a N_2 flow rate of 50 ml min^{-1}. TGA was conducted using a Perkin Elmer TGA4000 system. Both TGA curves and the first derivative of TG signals normalized with respect to initial sample mass have been used to analyze thermal properties.

2.4.3 | Differential scanning calorimetry (DSC)

DSC was performed using a Discovery DSC25 system of TA Instruments. A heating–cooling–heating cycle was

run on dry samples from 30 to 300°C at a heating/cooling rate of 20°C min^{-1}. Glass transition temperatures of modified starches were determined from the DSC curves as the inflection point of the endothermic change during the second heating run. Esterified starches were purified by sonication and dried in the same manner as described in section 2.3. DSC thermograms were collected for the purified samples and are provided in Figure S3 of the Supplementary material section.

2.4.4 | X-ray diffraction (XRD)

The diffraction pattern of the starch samples was recorded by powder XRD measurements performed between 5 and 65° 2θ angles with a Bruker D8 Advance X-ray diffractometer with increments of 0.02°. The wavelength of the Cu Kα radiation source used was 0.154 nm, generated at accelerating voltage of 40 kV and a filament emission of 40 mA.

2.4.5 | Scanning electron microscopy (SEM)

Secondary electron images were taken using a Philips XL30 ESEM at an acceleration voltage of 3 kV. Prior to imaging, all samples were placed on a carbon tape and sputter coated with a 15 nm layer of Au at 0.2 mbar using a Technics Hummer V Sputtering System.

2.4.6 | Karl Fischer titration (KFT)

To analyze the moisture content of the native and esterified starch samples, a Karl Fischer titration was used. All instruments were from Metrohm: 870 KF Titrino Plus along with 860 KF Thermoprep oven, with 803 Ti Stand as stirring unit. The titrant that was used was Hydranal 5 Titrant (Honeywell). Few mg of sample was added to a sealed vial and oven temperature was set to 110°C. Samples were subsequently lowered into the oven unit followed by a needle puncturing the sealed vial, extracting air and moisture content of the vial into the titration solution. Results were measured to give the actual moisture % of the samples.

2.4.7 | Proton nuclear magnetic resonance (^{1}H NMR)

Proton NMR analysis was done to determine the DS of esterified starch samples. For the solution state NMR, 10 mg of sample were dissolved in 1 ml of d_6 -DMSO at 85° C for 4 h, after which 600 µl of the supernatant were transferred into a 5-mm NMR tube and after that NMR measurement was performed on a 500 MHz Varian Unity INOVA NMR at 45°C. Starch samples were partially dissolved in the solution. Single pulse experiments were performed using 5 s relaxation delay, 3 s acquisition time and 128 scans. All spectra were processed by MestReNova 12.0 software.

2.4.8 | High performance liquid chromatography (HPLC)

To determine the DS, the modified starch polymers were saponified and then the released carboxylic acid content was analyzed by HPLC. 10 mg of dried sample were treated with 0.3 ml of MilliQ water and 1.2 ml of 0.8 M sodium hydroxide solution. The sample was heated and mixed overnight in a thermomixer (Eppendorf thermomixer comfort, Germany) at 70 °C. Thereafter the sample was allowed to cool down, followed by neutralization with 37% hydrochloric acid. The sample was centrifuged for 30 min at 14,100 rpm and room temperature. The supernatant was filtered through a 0.2 mm nylon filter. Quantification of the released acetic acid was performed by HPLC (Dionex Thermo Fisher, CA, USA) coupled with a UV detector (210 nm) using a Rezex ROA-Organic acid column (300 7.8 mm; Phenomenex, Torrance, CA, USA). The mobile phase was 2.5 mM sulfuric acid at a flow rate of 0.5 ml min^{-1}. Quantification was performed through calibration with carboxylic acid standards.

2.4.9 | N_2 physisorption

Nitrogen physisorption was measured using a Micrometrics ASAP 2420 apparatus at −196°C (−77 K) and the specific surface area was measured using the Brunauer–Emmet–Teller (BET) model. Prior to N_2 physisorption, the samples were degassed at 100° C for 24 h under N_2 atmosphere. Adsorption and desorption isotherms are provided in Figures S4 and S5 of the supplementary material section.

3 | RESULTS AND DISCUSSION

Potato starch was selected as a biorenewable starting material due to its wide range of modification and biodegradability and for the production of a sustainable polymer for potential packaging applications. Table 1 summarizes the yield of modified starches after supercritical CO_2 drying, their moisture content and DS after

TABLE 1 A summary of the DS of modified potato starch at different reaction times using citric acid as an organocatalyst at 120°C

Reaction time (h)	Yield (%) after supercritical CO_2 drying	Moisture content (%) by KFT	DS (titration)	DS (HPLC)	DS (^{1}H NMR)
Native starch	–	14.7	–	–	–
0.5	89	0.32	0.30	0.35	0.45
3	86	1.07	0.71	0.76	0.86
7	82	0.15	0.92	0.95	1.05

Note: All values were calculated after supercritical CO_2 drying.

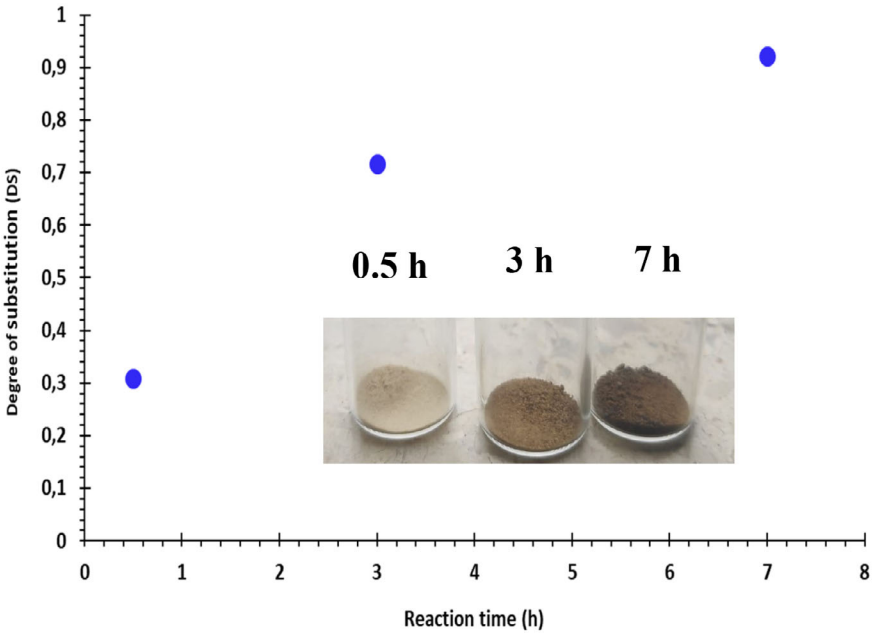


FIGURE 2 Influence of esterification time on the DS of potato starch. DS was determined by titration [Color figure can be viewed at wileyonlinelibrary.com]

starch esterification using the sustainable organocatalytic route.

From the data presented in Table 1, it can be observed that at 120°C in a sustainable environment, potato starch was successfully modified by esterification to produce starch esters with intermediate degrees of substitution ($0.2 < DS < 1.5$) finding potential applications in the polymers packaging industry. Furthermore, the moisture content was significantly reduced as determined by the KFT. This is attributed to the esterification reaction and the formation of ester groups in comparison to the old hydrophilic -OH groups that were present. However, this is not the only reason, because the samples were dried under supercritical CO_2 which has a high diffusion coefficient and results in efficient drying. As depicted in Figure 2, increasing the reaction time from 0.5 to 7 h resulted in a change in the color of starch from beige to light dark color to dark brown, which has been previously reported in literature by Emre et al.[18] upon increase in the DS from 0.30 to 0.92 as calculated from the back titration method. This might be attributed to slight degradation of starch in acetic anhydride environment.[18] Moreover, the DS values obtained from back titration and HPLC match quite well and are in reasonable agreement. Furthermore, DS values determined from ^{1}H NMR[20] as shown in Figure 3, the results obtained from this technique are limited to the starch fraction dissolved in DMSO at 85° C, since only the supernatant (dissolved fraction) was measured and analyzed by ^{1}H-NMR at 45° C. Figure 3 shows the three methyl protons of the acyl group at 2.04 ppm,[20] the DS was obtained from the integration of the acyl group compared to the hydroxyl group of starch. The technique is expected to overestimate the DS values due to the fact that a fraction of the starch (i.e. mainly amylopectin) is insoluble. In this work, esterified starches show additional resonances, indicating the presence of acyl protons. The spectrum of acetylated starches showed a methyl group signal at 2.10 ppm which is absent in the native starch sample. Additionally, solvent peaks from protiated solvent (not completely deuterated DMSO) also appear further downfield.

Figure 4 displays the images of native and acetylated potato starch granules (after supercritical CO_2 drying) by SEM. Figure 4a shows that native potato starch possesses

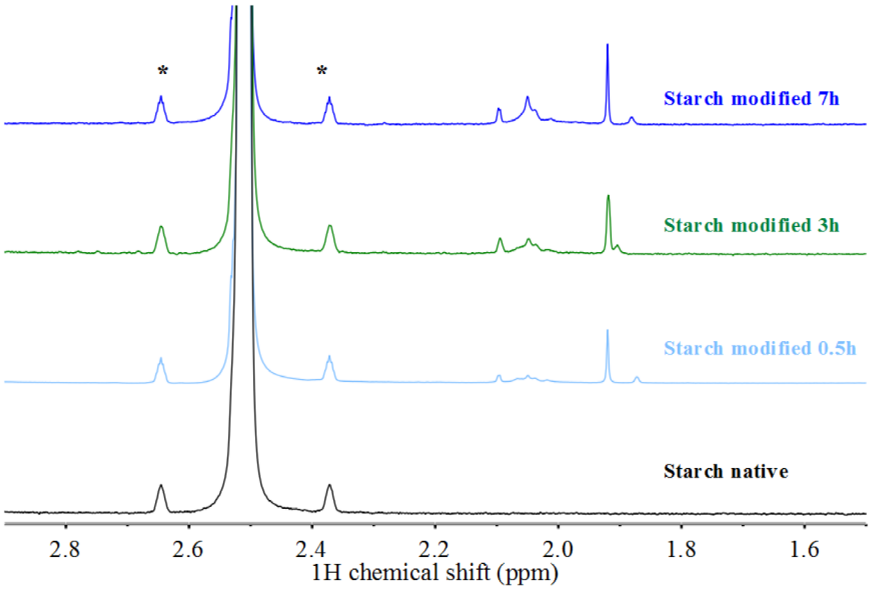


FIGURE 3 Normalized stack plot of the ^{1}H NMR spectra of potato starch samples: Native starch, 0.5 h modification, 3 h modification and 7 h modification. * represents the satellite transition peaks for d_6-DMSO. Peaks representing the modification groups on starch appear between 1.6 and 2.2 ppm [Color figure can be viewed at wileyonlinelibrary.com]

a smooth surface and that the granules are oval and unequal in size.[11,18] Upon esterification with citric acid the surface roughness has significantly increased as depicted in Figure 4b, c. This phenomenon might prove to be beneficial in increasing the interfacial adhesion of starch-polymer composites.[18] Additionally, the sample that underwent 7 h of acetylation (Figure 4c) appears to have coalescence between particles. This is different from what is expected to happen for acetylation under non-aqueous conditions, as coalescence and loss of granular structure is mainly attributed to the plasticizing effect of water and to a lesser extent by acetic acid prior to the esterification reaction.[18] The plasticization phenomena caused by water at temperatures higher than 90°C can result in the partial transformation of native starch into thermoplastic starch (TPS). The phase transition of starch plays a critical role in the plasticization of starch. The degree of phase transition also determines the processability and final product properties.[18]

The increased roughness of the surface could be an asset in adhesive properties of the starch. Moreover, these results are in line with what was reported for corn starch.[11,18]

Furthermore, the preliminary N_2 physisorption experiments carried on two dried samples (i.e., dried under vacuum at 80° C for 24 h and the other dried under supercritical CO_2 at 40° C, 100 bars for 2 h) that were modified for 0.5 h, showed significant differences in specific surface areas and mesopores volume. The sample dried under vacuum at 80° C had a specific surface area of ~0.76 m^2/g and a mesopore volume of ~0.001 cm^3/g. Meanwhile the sample dried under supercritical CO_2 had a specific surface area of ~2.87 m^2/g (i.e., ~ four times higher) and a mesopore volume of ~0.029 cm^3/g. These preliminary results are interesting and will be further explored in details in a future study.

In Figure 5, the FTIR spectra of the acetylated starches and native starch are depicted. To get confirmation of successful acetylation, spectra of acetylated starches are compared to the spectrum of native potato starch. First of all, there are various characteristic bands for native potato starch that should remain visible after modification. Furthermore, the location of the bands and its corresponding molecular groups will be explained. Between 3600 and 3000 cm^{-1}, a broad absorption band is measured and assigned to the vibration of hydrogen bonded OH groups.[11] This peak is very broad and is corroborated to the high hydrophilicity of native starch. It also becomes broader and less intense upon esterification (i.e. partial conversion of —OH groups to acetyl groups) due to the significant loss in hydrophilicity and increase in hydrophobicity.[18] Additionally, peak 4 at absorption band of 1634 cm^{-1} has been previously assigned to an amide group indicating protein content, which is usually less than 0.4% as has been reported earlier in the literature.[11,18] This peak disappears after esterification under acidic conditions as the proteins degrade and are removed upon washing during the purification steps.[18] However, this peak has been reported to be disputable.[11,18] Nevertheless, other authors state that this band indicates OH bending vibrations of water molecules.[11,19,20] These water molecules are believed to be adsorbed on the amorphous regions of starch granules.[21,22] This might be more likely, as all samples will still contain a small amount of water even if efficiently dried, which explains why the peak would be visible in the spectra of acetylated samples. Subsequently, at 2928 cm^{-1}, there is a band (peak 2) of medium intensity

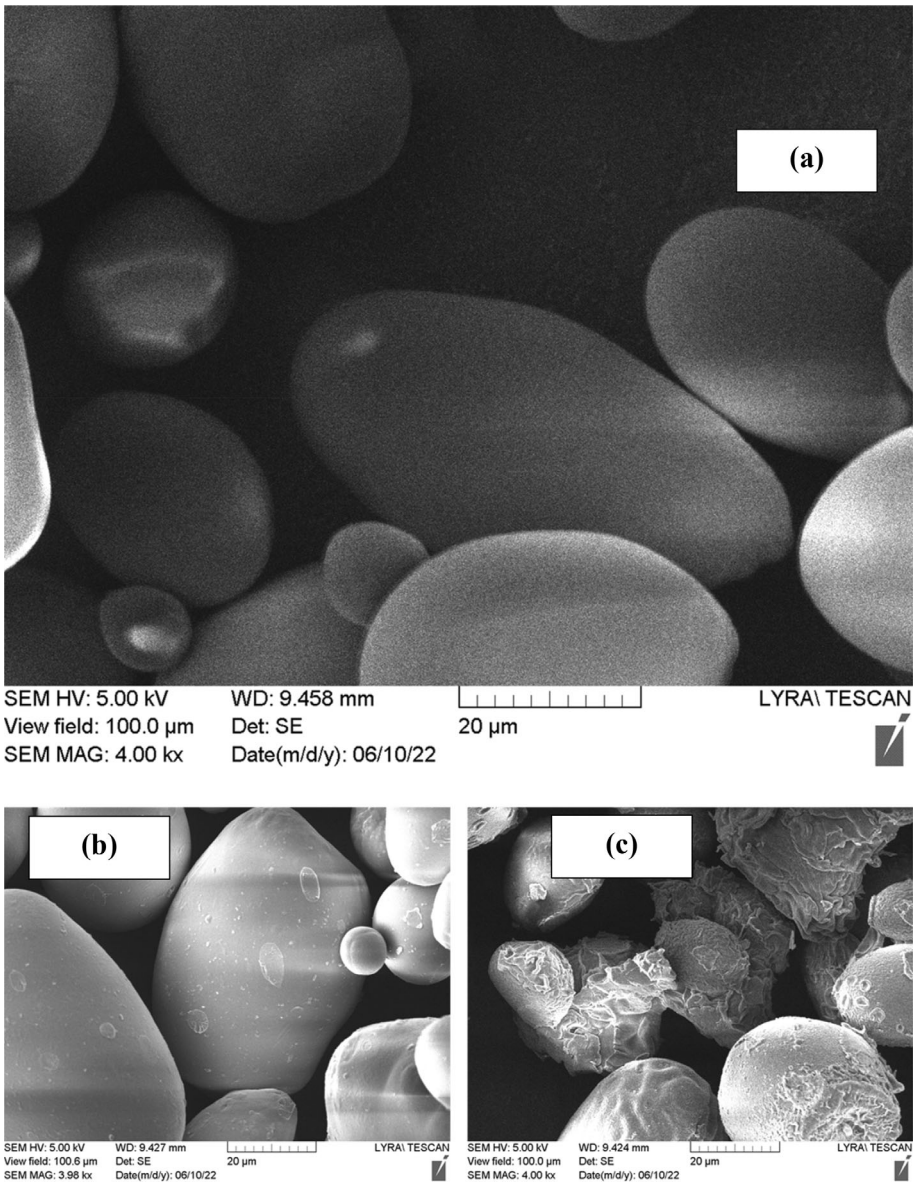


FIGURE 4 SEM images of (a) native potato starch, (b) 0.5 h acetylated starch, and (c) 7 h acetylated starch. All modified samples were dried under supercritical CO_2

which is attributed to a —CH stretching.[21] Then, between 1500 and 1300 cm^{-1} there are some bands that overlap: these bands can be assigned to vibrations that are typical of C—OH bending, CH_2 twisting and CH_2 bending.[11,22] Finally, there is a medium intense band at 1148 cm^{-1}, a small band at 1080 cm^{-1} and an intense peak at 1014 cm^{-1} corresponding to CO band stretching.[14]

Upon acetylation, three new bands should appear in the spectra. First, the intense band at 1740 cm^{-1} (peak 3) which corresponds to a C═O stretching.[11] This confirms the presence of species with an ester bond and thus confirms successful acetylation. It should be noted, however, that this stretching can also be attributed to species that are not part of the polymer backbone such as acetic anhydride and citric acid (CA) catalyst residue. This can be ruled out by comparing the FTIR spectra of the thoroughly washed CA samples (Figure S1) with the spectra of the same sample that was washed less thoroughly (Figure S2), as shown in the supporting information section. The intensities of the bands at 1740 cm^{-1} of the thoroughly washed samples are lower, suggesting that left over starting material has been removed after the second washing. Nevertheless, the appearance of the bands at 1370 cm^{-1} and 1230 cm^{-1} also confirm esterification as the former corresponds to asymmetric CH_3 vibration and the latter to a C—O stretching of an ester group.[11,21] As the DS increases, the area below the characteristic peaks should increase, i.e. the bands become more intense.[18] An additional indication of acetylation is the decrease in intensity of the peak between 3600 and 3000 cm^{-1}, suggesting a decrease in hydroxyl groups within the molecule and thus a decrease in hydrophilicity of the modified samples. In summary, the FTIR spectra proved that all samples showed signs of acetylation.

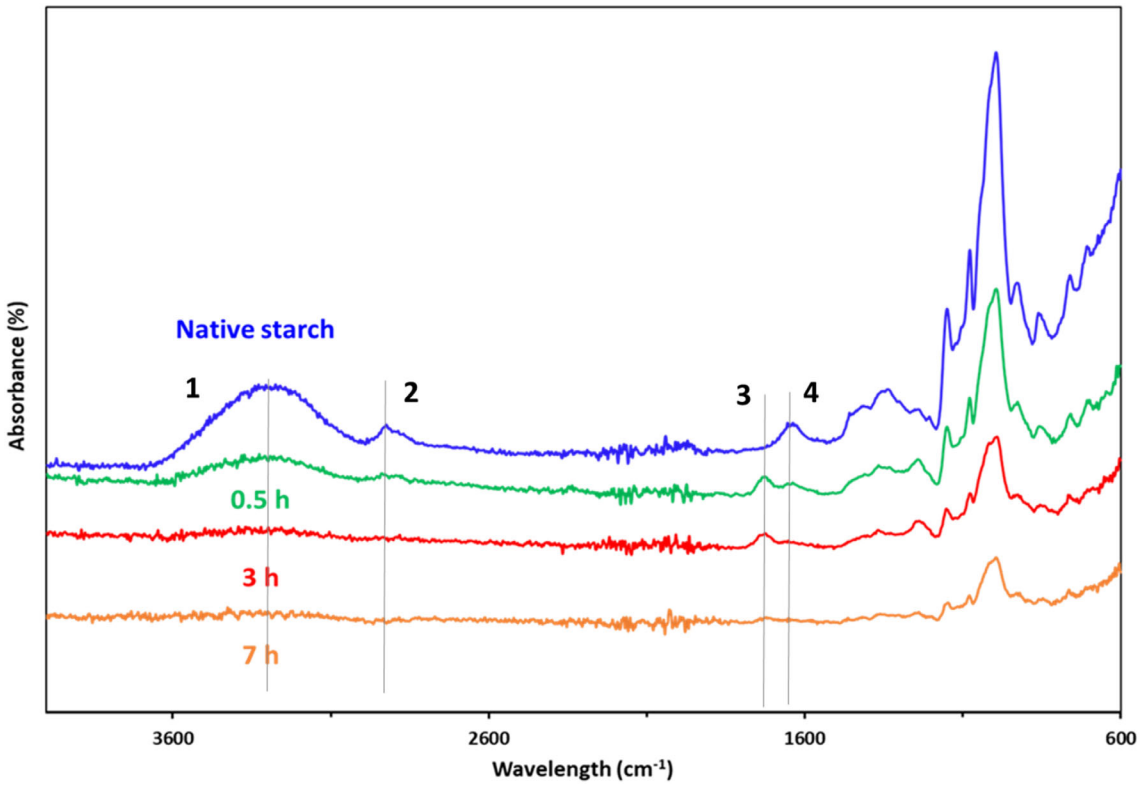


FIGURE 5 FTIR spectra of native and acetylated potato starches. All modified samples were dried under supercritical CO_2 [Color figure can be viewed at wileyonlinelibrary.com]

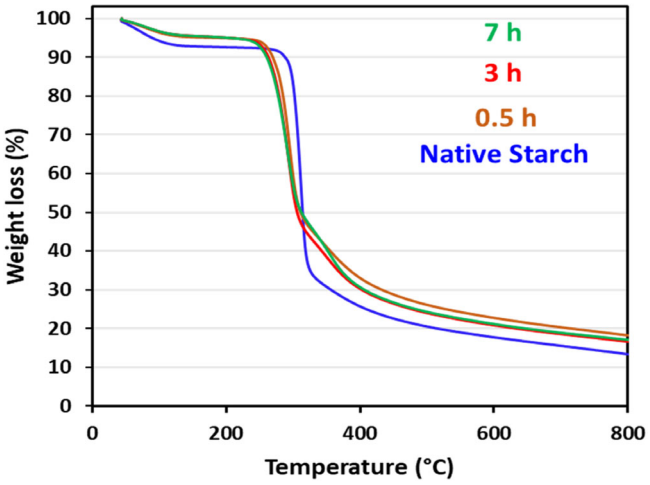


FIGURE 6 Thermal stability of potato starches explored by TGA. All modified samples were dried under supercritical CO_2 [Color figure can be viewed at wileyonlinelibrary.com]

The thermal analysis by TGA of all samples is depicted in Figure 6. Native starch shows only one step of weight loss at 300°C, which is attributed to the thermal degradation of starch (i.e. inter- and intramolecular dehydration reactions of the starch molecules with water as main product of decomposition).[11,18] Upon acetylation of native starch for 7 h, the decomposition temperature decreased slightly from 290 to 250° C as shown in Figure 6 in the main manuscript and from the derivative plot (DTG) in Figure S6 in the supplementary material section. This is attributed to the change in starch crystallinity from semicrystalline to amorphous as also will be confirmed later by XRD. Moreover, for the esterified starch samples, a second weight loss appeared at higher temperature (∼ 360° C) which could be assigned to the degradation of substituted anhydroglucose units, as previously reported in literature.[18] In summary, for packaging applications, the decomposition temperature of modified starch is still acceptable and the final product is thermally stable and resistant to water absorption (as confirmed by the KFT in Table 1) which does not make it the best environment for microorganisms and bacterial surface adhesion.

Additionally, DSC analysis of the three esterified starch samples is provided in the supplementary material section (Figure S3). From the DSC curves displayed in Figure S3 it is not easy to distinguish a clear endothermic step for all samples. For the 0.5 h CA and the 3 h CA sample, a T_g cannot be determined as a step in the DSC curve is barely visible. For the 7 h modified sample, it is possible to measure a T_g which was found to be ∼177° C. Imre et al. previously reported the increase in T_g upon the esterification of corn starch using acetic acid which

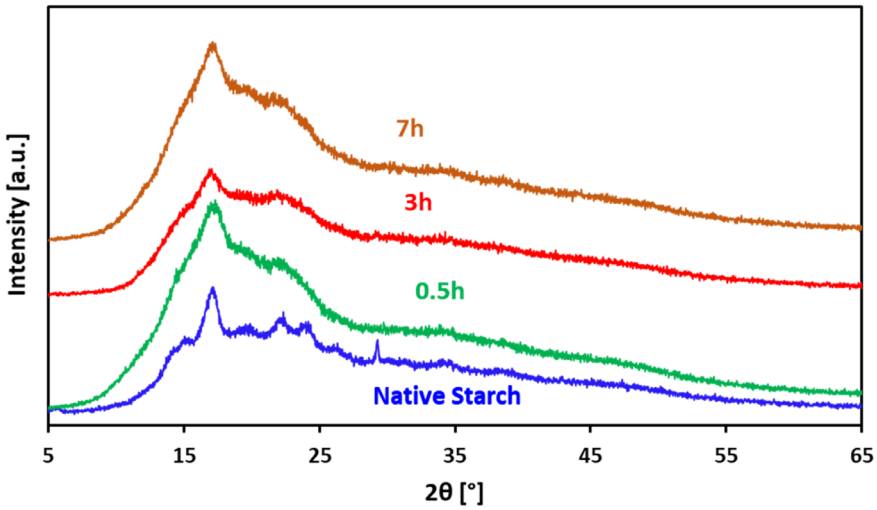


FIGURE 7 XRD patterns of potato starches showing loss of crystallinity upon acetylation. All modified starch samples were dried under supercritical CO_2 [Color figure can be viewed at wileyonlinelibrary.com]

was explained by the steric hindrance provided by the relatively bulky alkanoyl side group.[18] This means that the bulky groups prevent the chains from moving smoothly, increasing T_g.

In Figure 7 the X-ray diffractograms of native and acetylated potato starches are depicted. Native potato starch clearly shows a B type crystallite (i.e. hexagonal). There are characteristic peaks at 5.5°, 17°, 19.5°, 22°, and 24°. An extra peak can be observed at 15°, but this peak is not as intense as it would be for A type crystallites and is observed more often in potato starch.[23] It has been reported that crystallinity of corn starch decreases upon acetylation due to disruption of inter- and intramolecular forces.[23] If acetylation is performed via methods different from the organocatalytic route, crystallinity is destroyed at low DS values.[17] In the case of this investigation, using the organocatalytic route, the position and number of peaks seem to remain unchanged, despite the decrease in intensity.[11,18] When looking at the diffractograms it is clear that crystallinity is immediately lost upon acetylation. Additionally, acetylation takes place first on the amorphous domains followed by the crystalline domains. Furthermore, it has been recently reported that acetic anhydride seems to significantly alter the crystalline structure to a considerable degree due to its high reactivity as well as the potential plasticizing effect of its side-product, acetic acid.[18]

Additional data including N_2-physisorption (Figures S4 and S5) and derivative thermogravimetric analysis (DTG) (Figure S6) are provided in the supplementary material section.

4 | CONCLUSIONS AND FUTURE PERSPECTIVES

A novel esterification reaction for producing starch esters from potato starch has been explored. This process involved the use of benign organocatalyst, i.e. CA, acetic anhydride as esterifying reagent and potato starch as substrate. Intermediate degrees of substitution ($0.2 < DS < 1.5$) were targeted converting potato starch into starch esters that can find wide applications in the polymer industry. Moreover, the final products were efficiently dried using supercritical CO_2 which is an environmentally friendly fluid. The esterification procedure was free from toxic solvents. Different reaction times have been explored, varying from 0.5 to 7 h. Moreover, the influence of reaction time on the DS has been evaluated. This supercritical CO_2[24] drying process in comparison with conventional oven drying shall find potential applications in preserving the pores of the modified starch, hence not altering the final properties of the modified starch materials. Our future studies will include determining the DS, heterogeneity and local mobility,[25] degree of crystallinity[26] and solvent matrix interactions[27] of different modified starch-based materials from various origins using advanced[28] and beyond conventional solid-state NMR techniques,[29] a detailed economic study and analysis comparing various drying techniques, such as conventional oven drying, freeze drying, and supercritical CO_2 drying. Furthermore, the porosity of the final starch materials dried via the three different techniques will be compared and the mechanical properties of the materials will be further assessed. Additionally, the modeling of supercritical CO_2 drying of modified starch materials is currently an ongoing project.

AUTHOR CONTRIBUTIONS

Yasser A. Alassmy: Conceptualization (equal); formal analysis (equal). **Marwan M. Abduljawad:** Formal analysis (equal); resources (equal); visualization (equal). **Khalid M. Alshamrani:** Writing – review and editing (supporting). **Mohammed S. Alnafisah:** Data curation (supporting). **Mustapha El Hariri El Nokab:** Data

analysis (supporting). **Zahra Asgar Pour:** Investigation (supporting); methodology (supporting). **Diego R. Gomes:** Formal analysis (supporting). **Selin Yolcu:** Validation (supporting). **Khaled O. Sebakhy:** Conceptualization (lead); data curation (lead); formal analysis (lead); investigation (lead); methodology (lead); project administration (lead).

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

All data here are original data from the laboratory and have repeated multiple times to ensure reproducibility and accuracy.

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