Organocatalytic acetylation of starch: Effect of reaction conditions on DS and characterisation of esterified granules

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ABSTRACT

Starch acetates with varying degree of substitution (DS) were prepared by a novel solvent-free organo-catalytic methodology. The acetylation protocol involved a non-toxic biobased α-hydroxycarboxylic acid as catalyst, and proceeded with high efficiency in absence of solvents. The effect of reaction conditions including reaction temperature (90–140 °C), catalyst load (0–2.3 g/g starch), acetic anhydride/starch weight ratio (6.5–13.5 g/g), and starch moisture content (0.6–14.8%) on the DS of the esters was evaluated. The analysis performed showed that the increase of temperature and catalyst concentration resulted in higher DS values, and evidenced a beneficial contribution of native starch moisture content on the substitution level achieved. Variation of reaction conditions allowed starch esters to be obtained with DS in the 0.03–2.93 range. Starch esters were characterised in terms of morphology, chemical structure, thermal properties, and distribution in polar/non polar liquid systems.

1. Introduction

Starch is a naturally occurring, renewable, abundant, biodegradable polymer produced by many plants as a source of stored energy (Le Corre, Bras, & Dufresne, 2010). It is found in the form of discrete semi-crystalline granules in cereal grains, roots, tubers, stem-piths, leaves, seeds, fruit and pollen (Zavareze & Dias, 2011). Starch is utilised for its various functionalities in thickening, stabilizing, texturizing, gelling, film forming, encapsulation, water retention, shelf life extension, and coating and sizing among others (Lin et al., 2010; Miao, Jiang, Zhang, Jin, & Mu, 2011; Neelam, 2012). However, a number of industrial applications of starch are limited by some of its properties such as insolubility in cold water, loss of viscosity and thickening power after cooking, high tendency towards retro-gradation, water separation in starchy food systems upon retrogra-dation, high water sorption, poor stability and processing tolerance, low shear resistance, low thermal resistance, low flexi-bility of starch-based films, and low tensile property retention in aqueous environment (Cyras, Tolosa Zenklusen, & Vazquez, 2006; Parandoosh & Hudson, 1993; Shogren, 1996; Singh, Kaur, & McCarthy, 2007; Xie, Liu, & Cui, 2005). To overcome these and other shortcomings of native starch, physical, chemical and bio-technological modifications have been proposed (Neelam, 2012;

Xie et al., 2005). Among these, chemical modification of starch by esterification of some of its hydroxyl groups provides the polysac-charide with specific properties that allow its efficient use in food industry (i.e. as thickener, stabiliser, emulsifier and binder of frozen foods); in the pharmaceutical industry (i.e. filler, superdisin-tegrant and matrix former in capsules and tablet formulations), and in medicine (i.e. maintaining human colonic function and pre-venting colonic disease) (Bajka, Topping, Cobiac, & Clarke, 2006; Chowdary & Radha, 2011; Clarke et al., 2011; López-Rubio, Clarke, Scherer, Topping, & Gilbert, 2009; Phillips, Huijum, Duohai, & Harold, 1999).

Literature review shows that the route for starch esterification that has been studied most is the reaction of the polysaccharide in alkaline aqueous suspension with anhydrides as acylating agents and NaOH as catalyst (pH: 7–9) (Chi et al., 2008; Han et al., 2012; Singh, Chawla, & Singh, 2004; Xu, Miladinov, & Hanna, 2004). This is also the methodology currently used to com-mercially produce most starch esters with low DS. Drawbacks of this route include the production of large amounts of wastewater and sodium acetate by-product (Shogren, 2008). In this context, in a recent contribution of our group, we reported on the use of a novel organic-acid-catalysed heterogeneous route for the simple synthesis of starch esters, which is characterised by the use of a non-toxic green catalyst (i.e. tartaric acid), the absence of solvents, and the possibility of recovering the catalyst after reaction by simple evaporation/precipitation protocols (Tupa, Maldonado, Vázquez, & Foresti, 2013). In the referenced contribution, starch

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acetates and starch butyrates with varying ester contents (i.e. DS in the 0.06–1.54 interval) were prepared by the *sole* variation of reaction time (0.5–7 h). Other reaction conditions such as temperature, catalyst load, acylant/starch w/w ratio, and the starch moisture content, were kept at *fixed* values chosen based on an inspiring study dealing with the organocatalytic esterification of cellulose (Hafrén & Córdova, 2005).

As a continuation of the initial study described, in the current manuscript attention was focused on the effect that reaction conditions play on the substitution degree achieved in the organocatalytic acetylation of corn starch. In this context, reaction temperature, catalyst load, acetic anhydride/starch weight ratio, and the initial moisture content of starch were varied one at a time within selected intervals (i.e. 90–140 °C, 0–2.31 g catalyst/g starch, 6.5–13.5 g acylant/g starch, starch moisture content 0.6–14.8%), in esterifications carried out during a fixed reaction interval of 3 h. Previous contributions on starch acetylation performed by traditional methodologies (i.e. reaction with acetic anhydride in aqueous medium using sodium hydroxide as catalyst) (e.g. Han et al., 2012; Xu et al., 2004), and also by use of less conventional chemical routes (Biswas et al., 2008; Fang, Fowler, Tomkinson, & Hill, 2002; Shogren, 2008) have shown the importance of the previous parameters on the DS achieved during starch acetylation. However, to the authors' knowledge, this type of parametric study has not been previously performed for the organocatalytic route. Given the novelty of the system, the analysis carried out was aimed at increasing the knowledge on how reaction conditions can be manipulated in order to give starch acetates with the desired DS. The starch esters obtained were characterised in terms of morphology, hydrophobicity, chemical structure and thermal decomposition properties.

2. Materials and methods

2.1. Materials

Commercial native corn starch was kindly donated by Ingredion (Argentina). Acetic anhydride (97%) was bought from BioPack (Argentina). Hydrochloric acid (36.5–38%) and sodium hydroxide were reagent grade chemicals purchased from Anedra and BioPack, respectively. Potassium hydrogen phthalate and sodium carbonate were bought from Laboratorios Cicarelli and Mallinckrodt, respectively. L (+) tartaric acid was bought from Biopack. Petroleum ether 60–80 °C (i.e. ligroin, 0.67 g/ml) was obtained from Laboratorios Cicarelli.

2.2. Organocatalytic esterification

Acetic anhydride (6.5–13.5 g) and tartaric acid (0–4.62 g) were mixed in an oven-dried 100 ml glass flask equipped with a magnetic stir bar and a reflux condenser to prevent the loss of the anhydride. Temperature was then set at 115 °C for 5 min in order to achieve catalyst dissolution with continuous stirring. The homogeneous mixture was left to cool down to 40 °C and previously dried corn starch (2 g, 110 °C, 2 h) was added. The complete mixture was then heated to the desired temperature (90–140 °C) under continuous agitation in a thermostatized oil bath. In all cases esterification was run for 3 h. After that time, the mixture was allowed to cool down to room temperature, and the solid product was separated by vacuum filtration in a Buchner funnel. Several washings of the recovered solid with distilled water were performed in order to guarantee the removal of the catalyst and the unreacted acid. The solid was finally dried at 40 °C overnight. Assays were run in duplicate. Controls without tartaric acid were performed under identical conditions, aiming to evaluate the evolution of the uncatalysed reactions.

2.3. Determination of substitution degree

Substitution degree (DS) was determined by heterogeneous saponification and back titration with HCl, according to an adapted version of the standardised method used for determining the acyl content in cellulose acetate (ASTM D871-96, Standard Test Methods of Testing Cellulose Acetate). Briefly, 0.11 g of esterified starch was ground, dried at 105 °C for 2 h, and left to cool down in a desiccator. Dried samples were carefully weighted and transferred to 100 ml Erlenmeyer flasks to which 20 ml of ethyl alcohol (75%) was added. Flasks were heated loosely stoppered for 30 min at 50 °C. Afterwards, the suspensions were brought to slightly basic pH by addition of a few drops of 0.1 N NaOH using phenolphthalein as indicator. 20 ml of 0.1 N NaOH were then added to each flask, and heated again at 50 °C for 15 min. The flasks were finally allowed to stand tightly stoppered at room temperature for 48 h. At the end of this time, the excess NaOH present in the flasks was back titrated with 0.1 N HCl, using phenolphthalein as end-point indicator. A blank determination (native corn starch) was carried through the complete procedure. NaOH and HCl solutions were standardised using previously dried standard potassium hydrogen phthalate and sodium carbonate, respectively.

The acyl content was then calculated by:

$$\text{Acyl (\%)} = [(V_B - V_S) \times N_{HCl} \times M_{acyl} \times 10^{-3} \times 100]/W \qquad (1)$$

where V_B (ml) is the volume of HCl required for titration of the blank; V_S (ml) is the volume of HCl required to titrate the sample; N_{HCl} is the normality of the HCl solution; M_{acyl} is the molecular weight of the acetyl group (43.05 g/mol), and W (g) is the mass of sample used.

The DS of an acylated starch is defined as the number of hydroxyl (OH) groups substituted per anhydroglucose unit of the starch polymer. Since the anhydroglucose unit possesses three reactive hydroxyl groups, the maximum DS value is 3. The substitution degree of acetylated starches was calculated by:

$$\text{DS} = (162 \times \text{Acyl \%})/[M_{acyl} \times 100 - ((M_{acyl} - 1) \times \text{Acyl \%})] \qquad (2)$$

where 162 is the molecular weight of the anhydroglucose units.

2.4. Characterisation of starch esters

2.4.1. Scanning electron microscopy (SEM)

Drops of acetylated starches/water suspensions were deposited on microscope glasses and dried at 40 °C for 15 min. Samples were then coated with gold using an ion sputter coater, and observed at a magnification range of 5 and 10 KX by use of a scanning electron microscope Zeiss Supra 40 with field emission gun operated at 3 kV.

2.4.2. Hydrophobicity test

Native starch and acetylated starch samples (5 ± 0.5 mg) were qualitatively tested for hydrophobicity by placing them into transparent test tubes containing two immiscible liquid phases, i.e. 1.5 ml of petroleum ether (upper phase) and 1.5 ml of distilled water (lower phase). Depending on their DS, samples were expected to distribute preferentially in one of the liquid phases.

2.4.3. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectra of esterified starches were acquired on an IR Affinity-1 Shimadzu Fourier transform infrared spectrophotometer in transmission mode. Carefully dried (105 °C, 1 h) powdered samples of native and acetylated starches were mixed with KBr in a 1:20 ratio, and spectra were collected with 40 scans in the range of 4000–700 cm^{-1} with a resolution of 4 cm^{-1} (Singh, Nath, & Guha, 2011).

2.4.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of dried samples (5.5–6 mg, previously dried at 105 °C during 1 h) was conducted in a TGA-50 Shimadzu instrument. Temperature programs were run from 25 °C to 550 °C at a heating rate of 10 °C/min, under nitrogen atmosphere (30 ml/min) in order to prevent thermoxidative degradation (Rajan, Sudha, & Abraham, 2008).

3. Results and discussion

3.1. Study of the effect of reaction parameters on DS

In order to study the extent of starch modification at reaction temperatures lower than the one required for tartaric acid dissolution (i.e. 115–120 °C), the catalyst was firstly dissolved in the acylant at 115 °C, then the homogenous mixture was cooled down to room temperature to allow starch addition without aggregation, and finally the whole system was heated to the desired temperature value. With this protocol, reaction temperature was varied in the range of 90–140 °C , keeping all other reaction conditions at the values previously reported (Tupa et al., 2013). Results of the effect of reaction temperature on DS are shown in Fig. 1a.

As it is shown in Fig. 1a, in the 90–140 °C temperature range the extent of modification increased with reaction temperature,

leading to starch acetates with DS values in the 0.00–0.62 range. The increase of the DS observed as reaction temperature was increased may be attributed to a greater proportion of molecules with enough energy to react. Moreover, high temperatures surely contributed to increasing the swelling ability of starch as well as the diffusion rate of acetic anhydride. At 90 °C no evidence of reaction was observed. Considering that to improve binding, thickening, stability and texturizing the food industry requires starch acetates with DS in the 0.01–0.2 interval (i.e. those approved by the FDA – Food and Drug Administration), for these types of applications reaction temperatures within 100–120 °C could be of help. On the other hand, increasing the temperature level to 140 °C yielded starch acetates with a DS value of 0.62. Irrespectively of the reaction temperature used, in all cases starch acetates were recovered in granular form. Further reactions were carried out at 130 °C.

Aiming to reduce the amount of acylant used, (given its excess in the base conditions i.e. 21.4 mol/mol anhydroglucose), experiments with lower acylant/starch weight ratios were designed. However, considering that acetic anhydride acted as both reactant and solvent, the lowest volume of acylant used was limited by the possibility of keeping starch in suspension. The latter consideration limited the lowest acylant/starch ratio to 6.5 g/g starch (10.3 mol/mol anhydroglucose). In all assays the mass of starch used was the
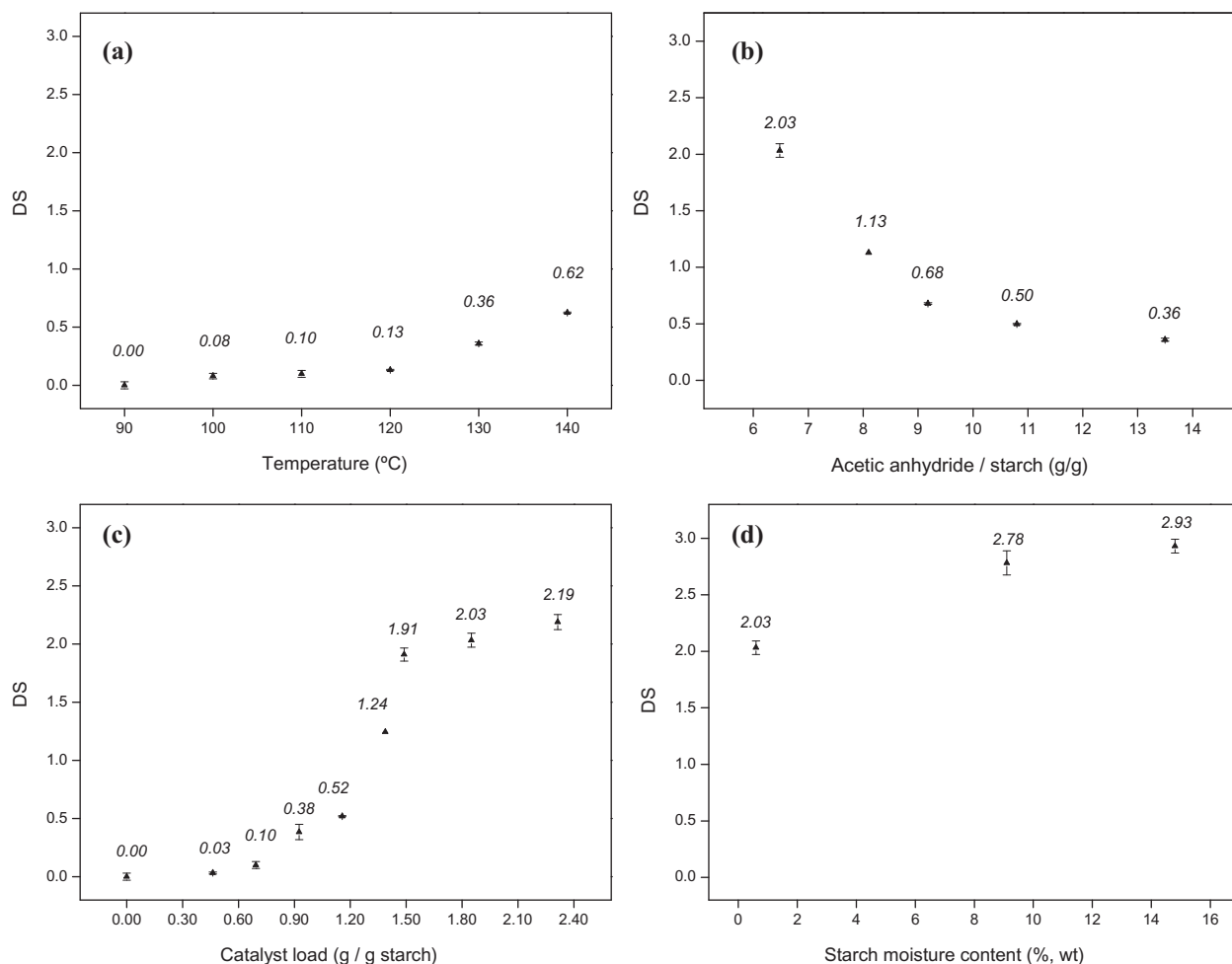
Fig. 1. Effect of reaction conditions on the DS of starch acetates, reaction time: 3 h, 2 g corn starch. (a) Effect of reaction temperature (1.85 g catalyst/g starch, 13.5 g acetic anhydride/g starch, starch moisture content: 0.6%); (b) effect of acetic anhydride/starch w/w ratio (130 °C, 1.85 g catalyst/g starch, starch moisture content: 0.6%); (c) effect of catalyst load (130 °C, 6.5 g acetic anhydride/g starch, starch moisture content: 0.6%); (d) effect of the moisture content of starch substrate (130 °C, 1.85 g catalyst/g starch, 6.5 g acetic anhydride/g starch).

same, i.e. 2 g. Fig. 1b summarises the DS values obtained for acylant/starch weight ratios in the 6.5–13.5 g/g interval. As it is shown, the reduction of the amount of acylant used promoted a huge increase in the level of substitution achieved.

Previous contributions on starch acetylation generally obtained starch esters with higher DS as the amount of acetic anhydride in contact with starch was increased. In the acetylation of high amylose (70%) maize starch with acetic anhydride using 50% aqueous NaOH as catalyst, Xu et al. (2004) observed that DS increased as the acetic anhydride/starch w/w ratio increased from 2 to 4 (from ≈2 to 2.7, respectively). These authors explained their results based on the hypothesis that high acetic anhydride concentrations resulted in a high molecular collision rate and also led to greater availability of acetic anhydride molecules in the vicinity of starch. The immobility of the hydroxyl groups made the acetylation reaction system essentially dependent on the availability of acetic anhydride molecules in the proximity of the starch molecules (Bayazeed, Farag, Shaarawy, & Hebeish, 1998). In a similar reaction system, Han et al. (2012) assayed the effect of lower acetic anhydride/starch w/w ratios (i.e. 0.0625–0.25 g/g) to find increasing DS values in the 0.066–0.160 interval. Results were also explained in terms of the number of collisions per unit of time between starch and acetic anhydride molecules which increased as the acylant concentration was augmented.

Using the current organocatalytic methodology, however, results evidenced increasing levels of starch substitution as acylant volume was reduced. The pattern observed may be explained in terms of the increase of catalyst concentration as acetic anhydride volume (used still in excess in order to solubilise the catalyst) was reduced. In contrast to conventional starch acetylations carried out in aqueous systems of constant volume, the current methodology is characterised by the use of no other solvent than the acylant itself, and thus lowering its volume resulted in higher catalyst concentration. The possibility of reducing the acetic anhydride volume while obtaining high DS levels appeared as very promising for the scaling up of the process. Aiming to minimise the amount of acylant consumed and also the waste stream volume, further assays were performed by keeping the acetic anhydride/starch w/w ratio at 6.5 g/g.

Keeping the acylant and the starch mass constant at the chosen values, DS was then tuned by varying the mass of catalyst used within the 0–4.625 g interval (i.e. catalyst load: 0–2.312 g catalyst/g starch). As shown in Fig. 1c the addition of higher catalyst amounts led to increasing levels of starch substitution, and starch acetates with DS as high as 2.19 could be obtained. However, data showed that once a DS value of 1.91 was achieved (catalyst load = 1.49 g/g starch), the use of a higher catalyst load did not lead to a significant increase in the substitution level achieved, and complete substitution of starch hydroxyls could not be reached. Results may be explained in terms of a hindered access of acetic anhydride to a fraction of hydroxyl groups which are not easily accessible for reaction. It is well-known that the reactivity to acylation of the three free OH groups of the anhydroglucose unit of starch decreases in the following order: primary C(6) OH > secondary C(2) OH > secondary C(3) OH. Location of secondary hydroxyl groups within the interior surface of starch forming hydrogen bonds with the OH groups on the neighbouring glucose units, make these hydroxyl groups less accessible for esterification, justifying the incomplete acetylation even at high catalyst and acetic anhydride concentrations. On the other hand, results showed that for food applications (DS 0.01–0.2), the catalyst load originally used could be significantly reduced. The absence of reaction when no catalyst was added was also demonstrated. In further assays, catalyst load was kept at 1.85 g/g starch.

The last variable assayed was the initial moisture content of starch. Considering the well-known negative effect of introducing

water in an esterification reaction system, in all the previous assays starch was carefully dried previous to its addition. Drying treatments at 110 °C for 2 h guaranteed a moisture content of 0.6%. The initial work on the organocatalytic esterification of cellulose by Hafrén and Córdova (2005) also recommended the use of cellulose sources that were dried overnight at 105 °C, as well as oven-dried glass vials. Similarly, in the acetylation of corn starch in the presence of Sc(OTf)$_3$ Shogren (2008), vacuum-dried corn starch (initial moisture content of native starch = 9.6%) was dried at 110 °C for 3 h before use. However, aiming to make the process simpler especially for scaling up interests, the effect on DS of using starch without previous drying (i.e. initial moisture content measured: 14.8%) was examined. Under the conditions detailed, a starch acetate with a DS of 2.93 (44% higher than the one achieved with almost anhydrous starch under identical conditions), was obtained. This result triggered the assay in reaction of a sample with intermediate moisture content. With this purpose a less severe drying treatment was designed, i.e. 1 h at 60 °C which led to a starch moisture content of 9.1% w/w. Results have been summarised in Fig. 1d.

Fig. 1d evidences that in the current reaction system the introduction of water through starch moisture content not only did not lead to a net reduction in the advance of esterification, but contrarily, higher substitution levels were achieved. The previous results can be explained in terms of the contribution of starch moisture to facilitating acylant penetration into the starch granules by swelling. In the acetylation of corn starch with acetic anhydride and Sc(OTf)$_3$ as catalyst, Shogren (2008) obtained starch acetates with low bulk DS (determined by ^{1}H NMR) but high surface DS (XPS measurements). The author attributed the DS combination found to the low permeability of starch granules to acetic anhydride in an acetylation methodology in which there was no water present to swell the hydrogen bonded starch network. Similarly, results summarised in Fig. 1d could be explained in terms of a beneficial net effect of starch humidity, by promoting the anhydride entrance into starch granules and the encounter with less accessible OH groups. The possibility of avoiding starch drying seemed very interesting for making the scaled up process easier and improving its economy.

3.2. Characterisation of starch acetates

Starch acetates samples resulting from the parametric analysis detailed in Section 3.1. were characterised by use of Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Samples were also qualitatively evaluated for hydrophobicity upon observation of their distribution in biphasic liquid systems containing polar/non polar phases. For the sake of brevity, characterisation results included below are only illustrated for esters obtained by the assay of acylant/starch w/w ratio, i.e. DS = 0.36, 0.50, 0.68, 1.13, 2.03.

Fig. 2 compiles SEM micrographies of acetylated starch granules with increasing DS. As it is shown, the smooth surfaces of native corn starch granules (Fig. 2a and b) turned into rougher surfaces when the degree of starch substitution reached DS = 0.36 (Fig. 2c and d). The increment of roughness of the granules' surface upon acetylation has been previously reported (Singh et al., 2004; Tupa et al., 2013). As the esterification level increased to DS = 0.50, starch acetate granules still exhibited rough surfaces and in some granules deformed depressed zones were observed (Fig. 2e and f). For starch acetates with DS = 1.13 single grooves appeared in most granules, and in some of them the interior could be seen (Fig. 2g and h). A similar phenomenon was observed in acetylated starch granules with DS higher than 0.56 obtained by the same methodology by the sole variation of reaction time (0.5–7 h, Tupa et al., 2013). Deformation and fissuring observed in acetylated
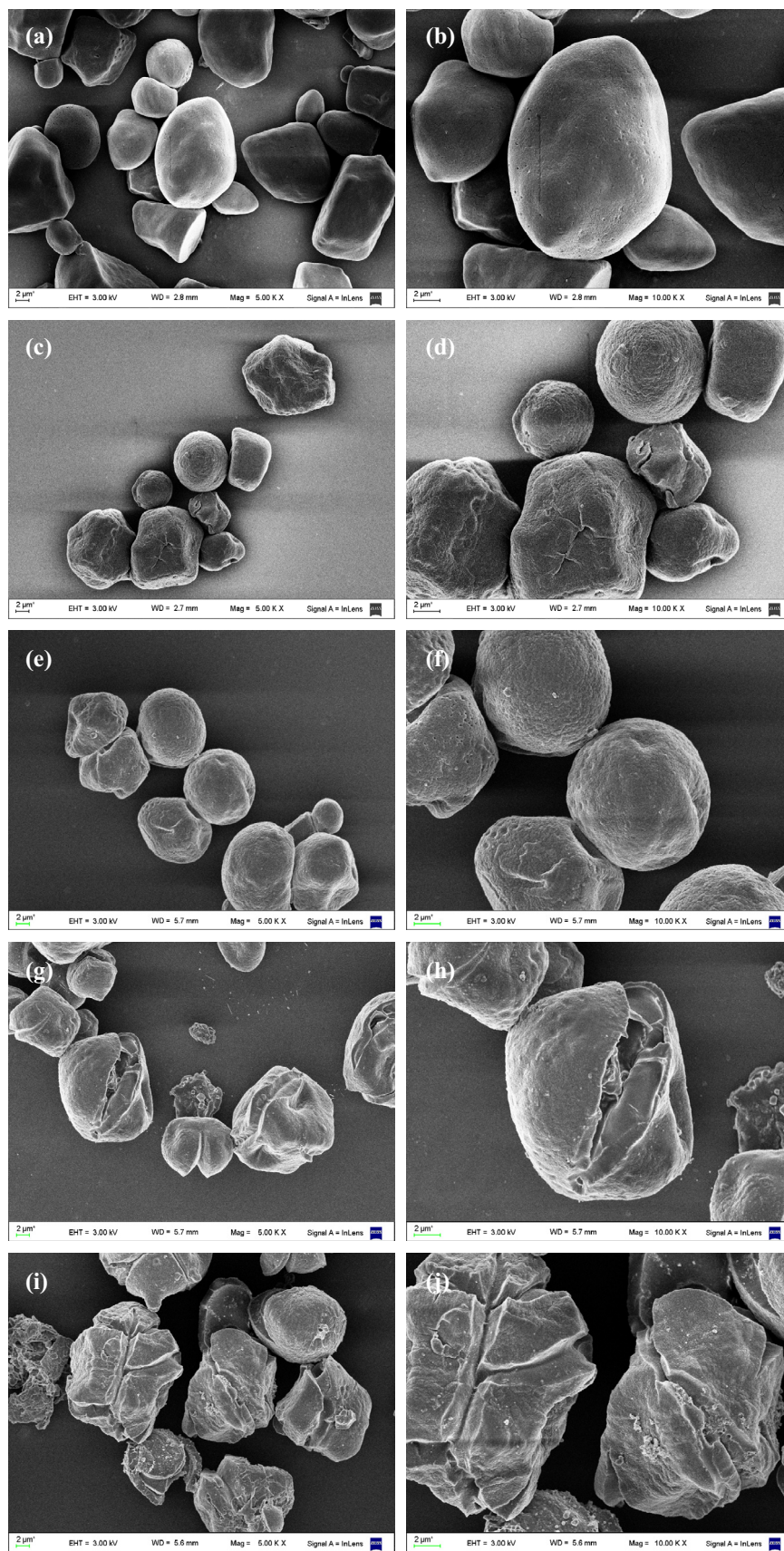
Fig. 2. SEM micrographies of native and acetylated corn starches with increasing DS. (a and b) Native starch; (c and d) DS = 0.36; (e and f) DS = 0.50; (g and h) DS = 1.13; (i and j) DS = 2.03. Magnification: left: 5KX, right: 10KX.

starch granules at high DS might have been caused by the disruption of inter- and intra-molecular hydrogen bonds induced by the progressive replacement of OH groups by less polar acetate groups, resulting then in a weaker granular structure of starch. The increased fragility of acetylated granules exposed to constant magnetic stirring could thus have led to the observed changes in starch morphology. Besides this, the progressive replacement of hydroxyl groups by more voluminous acetate groups might also have contributed to the fissuring of highly substituted starch granules. Esterified starch granules with DS = 2.03 exhibited multiple and generally deeper grooves, and a submicron granulated coating appeared in some of the particles (Fig. 2i and j). The area covered by the caster increased for starch acetates with still higher DS, i.e. DS = 2.93 (data not shown). In contrast to other starch acetates with such high DS, no loss of the granular structure of starch was observed.

Starch acetates were qualitatively tested for hydrophobicity in test tubes containing equal volumes of distilled water and petroleum ether (0.67 g/ml). When added to the biphasic system, native starch fell to the lower aqueous phase, absorbed water and sank immediately to the bottom of the test tube. Contrarily, starch acetates fell across the non polar phase and remained floating in the non-polar/polar interphase. Test tubes were then vertically shaken and once liquid phases became separated, the distribution of the solids in the immiscible phases was observed. As illustrated in Fig. 3, hydrophilic native starch distributed in the lowest aqueous phase, which turned opaque (Fig. 3a). On the other hand, acetylated starches preferentially remained in the lowest zone of the upper organic phase and did not reach the bulk aqueous phase (Fig. 3b–f). Despite its simplicity, the described assay qualitatively evidenced the change in starch surface polarity induced upon acetylation.

The chemical structure of native and acetylated starch samples was studied by means of Fourier transform infrared spectroscopy. The collected spectra are included in Fig. 4. FTIR spectra of starch acetates showed bands characteristic of the chemical structure of the polysaccharide, i.e. stretching of hydrogen bonded O–H groups ($3700-3000\ cm^{-1}$), C–H stretching modes ($3000-2800\ cm^{-1}$), O–H bending vibration of adsorbed water molecules ($1642\ cm^{-1}$), C–O–H bending, CH_2 twisting, CH_2 bending and C–O–O stretching ($1500-1300\ cm^{-1}$), CH_2OH (side chain) related mode/ C–O–H deformation mode ($1240\ cm^{-1}$), coupling mode of C–O and C–C stretching ($1158\ cm^{-1}$), C–O–H bending mode ($1084\ cm^{-1}$), C–O
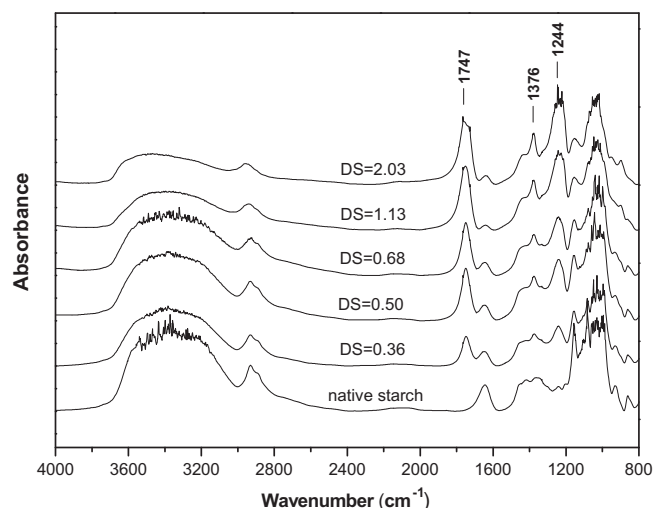

Fig. 4. FTIR spectra of acetylated starches, DS: 0.36–2.03. A native starch spectrum is also included for comparison purposes.

band stretching ($1055\ cm^{-1}$), skeletal mode vibrations of the α-1,4 glycosidic linkage ($923\ cm^{-1}$), C–H and CH_2 deformation ($857\ cm^{-1}$), and C–C stretching ($763\ cm^{-1}$) (Cael, Koenig, & Blackwell, 1975; Cyras et al., 2006; Diop, Li, Xie, & Shi, 2011; Garg & Jana, 2011; Kizil, Irudayaraj, & Seetharaman, 2002; Santha, Sudha, Vijaykumari, Nayar, & Moorthy, 1990; Xu et al., 2004;).

FTIR spectra of starch esters additionally showed bands of varying intensity attributable to the esters groups introduced, i.e. stretching of the C=O of the ester group ($1747\ cm^{-1}$), CH_3 deformation vibration of the ester moiety ($1376\ cm^{-1}$), and C–O–C stretching vibration of the ester moiety ($1244\ cm^{-1}$) (Biswas et al., 2008; Diop et al., 2011; Han et al., 2012; López-Rubio et al., 2009). The intensity of those bands increased with the esterification level, whereas the intensity of the band assigned to the stretching of hydroxyl groups of starch ($3700-3000\ cm^{-1}$) gradually decreased as a consequence of the increasing number of hydroxyls which were replaced by ester groups.

All starch acetates synthesised were further analysed in terms of their thermal decomposition pattern when heated at a constant
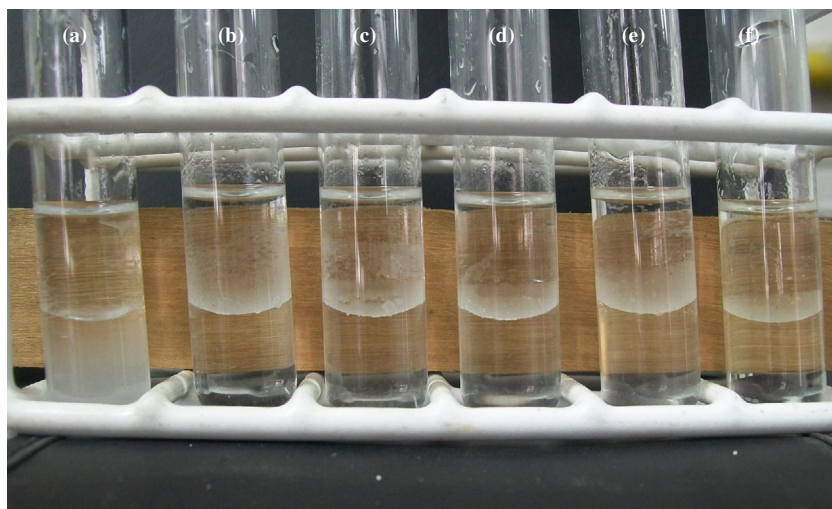

Fig. 3. Photograph showing the distribution of native and acetylated corn starches with increasing DS in distilled water/petroleum ether mixtures. (a) Native starch; (b) DS = 0.36; (c) DS = 0.50; (d) DS = 0.68; (e) DS = 1.13; (f) DS = 2.03.

rate (10 °C/min) in the 25–550 °C range. Fig. 5 summarises results for samples with DS in the 0–2.03 interval. Data are presented in terms of the first derivative of TG signals (DTG), normalised with respect to the initial sample mass, and moved in the y axes for clarity purposes.

For native starch, thermogravimetric analysis revealed two weight losses which correlated with two peaks in the lowest DTG curve included in Fig. 5. The first weight loss (6.5%) was observed in the 25–145 °C temperature range and it is attributed to the release of physically adsorbed and hydrogen bonded water that remained in starch even after preconditioning. The second weight loss (73%) took place in the 270–365 °C temperature range and was assigned to starch decomposition. The decomposition of starch is a result of inter and intramolecular dehydration reactions of starch molecules, with water as a main product of decomposition (Thiebaud et al., 1997).

On the other hand, acetylated starch samples with DS in the 0.36–1.13 interval showed three weight losses, i.e. the one attributed to starch dehydration, the one attributed to the condensation of remaining hydroxyl molecules with water as a main product of decomposition, and an extra high temperature decomposition peak in the 345–415 °C interval. This high weight loss has previously been attributed to evolving acetic acid from acetates decomposition (Elomaa et al., 2004; Tupa et al., 2013). With the increase of the DS of the samples, the area of the peak attributed to the condensation of remaining hydroxyl molecules decreased in favour of the increase of the acetates decomposition peak. Linear correlation of the percentage area of the latter peak with DS of starch acetates has been reported previously (Elomaa et al., 2004; Tupa et al., 2013). With the increase of DS, data included in Fig. 5 also suggests the occurrence of some degradative reactions of starch, which could be responsible for the movement of the starch decomposition peak to lower temperatures. The existence of degradative reactions during starch acetylation has previously been proposed by Shogren (2008) in the esterification of corn starch using acetic anhydride and Sc(OTf)$_3$ as catalyst (80 °C, 1 h, surface DS: 1.2). In the current system, as starch acetates with higher DS were obtained samples developed a beige colour of increasing intensity.

The upper DTG curve included in Fig. 5 corresponds to a starch acetate sample with a DS value of 2.03. As it is shown, for this sample the two first peaks previously described for starch acetates with lower DS had a very low contribution to mass loss as a consequence of the lowest number of OH groups remaining in starch. In

fact, the percentage mass loss for the hydroxyl groups condensation peak accounted for 12%, whereas mass loss due to acetate decomposition was 72%. The peak attributed to the decomposition of the acetate groups introduced was centred at 383 °C, a temperature value almost 60 °C higher than the temperature at which the maximum weight loss rate occurred for native starch (i.e. 325 °C). This result is in accordance with most literature devoted to starch acetates' characterisation, which reports that esterification resulted in increased thermal stability, as evidenced by single DTG peaks that occured at higher temperatures than the one found for native starch decomposition (Xu et al., 2004). The increase in thermal stability of acylated starches has been frequently attributed to the lower number of hydroxyl groups remaining after esterification (Fang et al., 2002; Xu et al., 2004). The evolution of DTG curves shown in Fig. 5 for starch samples within the 0–2.03 DS interval clearly illustrates how the reported increase in the thermal stability of esterified starch was achieved, as OH groups were gradually replaced by more thermally stable acetate groups.

4. Conclusions

The effect of reaction conditions on the organocatalytic acetylation of corn starch was studied. Data gathered demonstrated that the increase of reaction temperature and catalyst concentration had a positive effect on the degree of starch substitution achieved. Moreover, the study performed showed that the amount of acylant used in the initial studies could be significantly reduced, and that the methodology does not require the previous drying of starch. Both results are highly encouraging for reducing the cost of the methodology, especially in view of scaling up purposes. The study performed also evidenced the versatility of the acetylation route developed, which can be used to obtain starch acetates with controlled substitution level within the whole DS range just by adequate selection of reaction conditions.

Characterisation of starch esters evidenced that although some grooves appeared on starch acetates of high DS, the granular structure of the polysaccharide was not lost upon acetylation. Results also showed that the increase of DS resulted in starch granules with higher affinity for non-polar liquid phases, and much higher thermal stability than native starch.

The possibility of easily obtaining starch acetates with controlled substitution degree (0.03–2.93) in short time intervals and under relatively moderate conditions, suggests that the organocatalytic methodology is a promising non conventional route for the synthesis of starch esters with specific properties.

Acknowledgements

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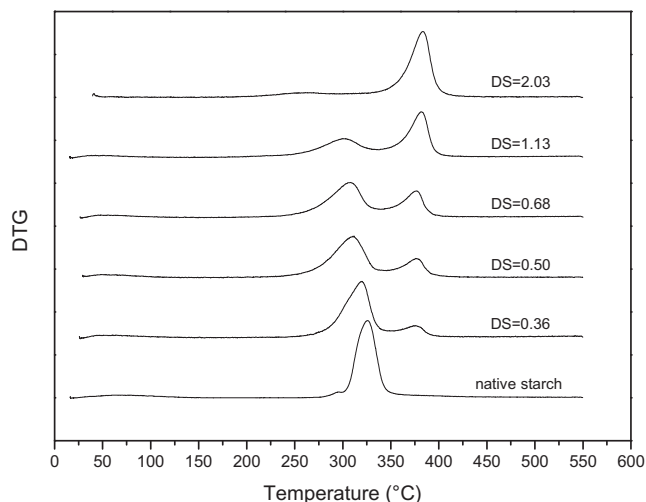

Fig. 5. DTG curves for acetylated starches, DS: 0.36–2.03. A native starch spectrum is also included for comparison purposes.

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