Influence of the Glycerol Content and Temperature on the Rheology of Native and Acetylated Starches During and After Gelatinization

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ABSTRACT: Native potato starch was acetylated and characterized. The influence of this chemical modification on different properties of the starch was studied. The characterization included the molecular weight, thermal properties, crystallinity, amylose content, swelling behavior, and pasting and rheological properties. The chemical modification induced small changes in the crystallinity of the starch and a reduction in the gelatinization heat and in the range of temperatures at which it took place. The amylose content was determined for acetylated and native potato starches. The swelling of native granules was higher than the swelling of acetylated potato starch. Regarding pasting behavior, the native and acetylated starches responded in similar ways to changes in the temperature and glycerol content. Finally, the acetylated starch was less pseudoplastic than the native starch. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3410–3420, 2011

Key words: biopolymers; modification; rheology

INTRODUCTION

Starch is one of the most abundant polysaccharides. It is the main form of energy storage in plants and can be very easily extracted. Starch is composed of a mixture of (1→4)-α-d-glucopyranosyl units in the form of linear amylose and highly branched amylopectin. These two molecules are arranged as highly ordered and densely packed chains organized within insoluble granules.

Branching in amylopectin occurs because of infrequent (1→6)-bonds in the polymer structure. In addition, small quantities of lipids and proteins are present.[1,2] Potato starch is more anionic than other starches because it has a phosphate group in the sixth positions of the d-glucose units of amylopectin.[3]

Native starch is semicrystalline and has a crystallinity of 20–35%. Amylopectin is the main crystalline component in granular starch amylopectin is the main crystalline component in granular starch. The crystalline regions are arranged as lamellar domains consisting of double helices of the amylopectin outer chains. Additional crystallinity may arise from cocrystallization, with amylose crystallization resulting in a single-helix structure.[4]

Singh et al.[5] stated that "gelatinization starts at the hilum of the granule and swells rapidly to the periphery." Gelatinization occurs initially in the amorphous regions, as opposed to the crystalline regions, of the granule, because hydrogen bonding is weakened in these areas." The loss of crystallite order during gelatinization occurs when starch suspensions are heated in the presence of water.[6–9] Donovan[10] studied wheat and potato starches and reported that for water concentrations higher than 30 wt %, the amorphous regions of the granules absorb water and swell. When the water/starch ratio exceeds 70%, all the crystallites are pulled apart by the swelling process. Therefore, no crystals will remain after the gelatinization process is completed.

This generates quite unusual rheological behavior. Many studies can be found in the literature, but the

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results are fairly dissimilar. Thus, the generalization of starch rheology is not an easy task because many different formulations, depending on the final uses of the starch-based materials, have been studied. The type and concentration of the starch as well as the use of plasticizers greatly affect its behavior. Highly concentrated dispersions of poorly swollen granules at low temperatures often show dilatant or shear-thickening behavior, whereas more dilute suspensions of highly swollen granules at higher temperatures show characteristic pseudoplastic or shear-thinning behavior.[11] Several researchers have studied the rheology of starch and starch gelatinization with different equipment and experimental setups.[12–22] Rodriguez-Gonzalez et al.[23] and Willet et al.[24] found that starch suspensions exhibited power-law behavior. They reported that the viscosity (η) of the suspensions decreased with increasing temperature and moisture content. The power-law index increased with increasing temperature, whereas the consistency index (K) decreased with increasing temperature and increasing moisture content. Similarly, Aichholzer and Fritz[25] found that a more intense degree of destructurization caused a parallel shift of the η functions to reduced η levels. This may have been due to a remarkable reduction in the remaining nondisintegrated starch particles. They also studied the influence of the glycerol content (G) on η of starch suspensions and found that it could be described by an exponential shift similar to that found for the temperature. The authors proposed a combined shift factor considering the influence of both the temperature and the plasticizer content on η of thermoplastic starch. Della Valle et al.[26] investigated the influence of the starch structure on its rheological behavior. They compared starches from different botanical sources and found important differences among them, which were attributed to molecular features such as the molecular chain length and linearity.

Regarding the acetylation of starch granules, esterification with acetyl groups changes the stability of starch and increases its resistance to retrogradation.[27,28] Moreover, many authors have reported different effects caused by acetylation. Rutemberg et al.[29] reported increases in the swelling and solubility of starch granules due to the incorporation of acetyl groups. Adebowale et al.[30] reported a lower degree of swelling and partial depolymerization due to modification by acetylation. In addition, López et al.[31] found that acetylated starch presented a lower amylose concentration but a higher degree of polymerization in comparison with native starch. Fringant et al.[32] reported differences in water absorption and mechanical properties with the degree of acetylation.

Although several publications deal with the mechanical properties of acetylated starch,[33,34] there are not many publications concerning the rheological properties of acetylated potato starch in comparison with other starch types.[34–36] Singh et al.[35] and Lee and Yoo[36] found that the acetylation of corn and potato starch decreased the transition temperatures and enthalpy of gelatinization. Acetylated starches showed higher storage and loss modulus peaks and lower tan δ values than their counterpart native starches upon heating.

The aim of this work was to study the influence of chemical modification on the structure and properties of potato starch. In addition, the influence of acetylation, temperature, and glycerol content on the rheological behavior of native and acetylated potato starches was studied.

EXPERIMENTAL

Materials

Native potato starch was kindly provided by Avebe (Buenos Aires, Argentina). Glycerol and acetic acid (both analytical grade) were purchased from Cicarelli (Buenos Aires, Argentina). Purified potato amylose and amylopectin from Sigma–Aldrich (St. Louis, MO) were used.

Acetylation method

Potato starch was acetylated according to the following procedure.[33] Starch (15 g) was immersed in a solution of acetic acid (80 mL), toluene (100 mL), and perchloric acid (0.5 mL) at 25°C for 4 h. The starch was washed carefully to remove excess acid and then was kept at pH 7 by the addition of small amounts of a solution of NaOH. The ester content was determined in a previous work[33] to be 1.7. The reaction is shown in Figure 1.

Infrared spectroscopy

Powder starch was dried in a vacuum oven for 24 h. Starch acetylation was verified by Fourier transform infrared (FTIR) spectroscopy. The drift method was used; wavelengths were evaluated from 400 to 4000 cm^{-1}. Spectra were normalized according to the intensity of the peak at 2933 cm^{-1}, which corresponds to the CH_2 group.

Differential scanning calorimetry (DSC) measurements

DSC analyses were carried out with a Shimadzu DSC-50 (Kyoto, Japan) from room temperature to 110°C at a heating rate of 10°C/min under a nitrogen atmosphere (20 mL/min). So that gelatinization could take place, water was added to the samples.

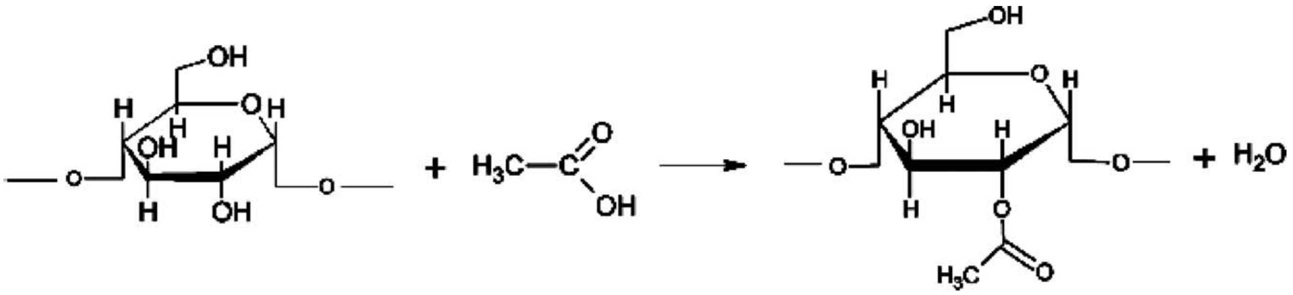


Figure 1 Starch acetylation reaction.

According to Donovan,[10] the water content needed to be greater than 70% to prevent superpositioning of the gelatinization and melting peaks. Sealed caps were used to prevent water evaporation during tests.

Determination of the amylose content by photospectroscopy

The blue method described by McCready and Hassid[37] was used for determining the amylose content of native and acetylated starches.

Purified potato amylose and amylopectin were used. One hundred milligrams of amylose and amylopectin were dissolved for 18 h at room temperature in 9 mL of 1*N* NaOH and 1 mL of 95% ethanol with separate flasks. After dissolution, distilled water was added to bring the volume to 100 mL. Solutions with 0, 10, 20, 25, and 30% concentrations were prepared via the mixing of appropriate amounts of 100% amylose and 100% amylopectin solutions. Subsequently, 5 mL of each solution was poured into different flasks containing 50 mL of distilled water; 1 mL of 1*N* acetic acid and 2 mL of iodine reagent (0.2 g of iodine and 2 g of potassium iodide in 100 mL of distilled water) were added. More water was added to bring the volume to 100 mL. Solutions containing native and acetylated starches were prepared with the same procedure.

The absorbance at 620 nm was measured after 20 min with an Agilent 8453 (Santa Clara, CA) spectrophotometer. The amylose content was determined by a direct comparison of the calibration curve and the results for the native and acetylated starches.

X-ray diffraction (XRD) characterization

Native and acetylated starch powders were investigated by X-ray scattering with a Philips PW 1830 (Amsterdam, The Netherlands) X-ray device ($2\theta = 5$–60) with Cu Kα radiation at room temperature and a scanning rate of 1°/min. Starch powders were previously dried in a vacuum oven at 35°C for 48 h. The crystallinity was determined as the ratio of the crystalline area to the total area.

Optical microscopy

The gelatinization process was studied with optical microscopy through the evaluation of the evolution of starch granules during heating. Cross-polarized light was used to reveal the existence of ordered zones (birefringence). An Olympus SZH 10 (Tokyo, Japan) optical microscope was used.

The swelling degrees of both types of starches were evaluated with a hot-stage add-in for the microscope. Heating/holding cycles were applied to vacuum-dried powder. The heating rate was set to 10°C/min from 25 to 55°C, and then the heating rate was decreased to 1°C/min from 55 to 63°C; finally, a holding time of 10 min at 63°C was used until complete gelatinization was reached. The gelatinization temperature was determined by DSC as stated previously. Pictures were taken at the following specified time intervals: 0 min (25°C); 3 min (55°C); and 11, 13, 15, 17, 19, and 21 min (63°C). The projected areas of five individual granules for each sample (native and acetylated) were measured before, during, and after gelatinization. The ratio was related to the ability of a granule to adsorb water within its structure. To be able to focus on single granules, a diluted concentration was used (0.1 g of starch in 5 or 10 mL of water).

Preparation of the samples for η measurements

The samples were prepared via the mixing of different quantities of starch, glycerol, and distilled water. In all cases, the starch content was fixed at 33 wt % with respect to the total sample weight; a plasticizer (glycerol and water) at the concentration of 67 wt % was added. Glycerol was added as a part of the starch content. Finally, water was added to complete the remaining 67 wt % of the plasticizer. Table I shows the composition of each sample.

Viscosity measurements

A Brookfield HV-DII+ (Middleboro, MA) cone and plate rotational viscometer was used. This configuration required small samples and allowed us to

TABLE I
Samples Composition (wt %) with a Constant Plasticizer Content of 67 wt % (Glycerol + Water)

Starch type	Starch/total (wt %)	Glycerol/starch (wt %)	Glycerol/total (wt %)	Water/total (wt %)
Native	33	25	8.25	58.75
	33	33	11.0	56.00
	33	50	16.5	50.50
Acetylated	33	25	8.25	58.75
	33	33	11.0	56.00
	33	50	16.5	50.50

control the temperature and evaporation of water. To study the effect of temperature, native and acetylated starch samples with a glycerol concentration of 25% (w/w_{Starch}) were evaluated at three different temperatures (65, 75, and 85°C). Afterwards, native and acetylated starch samples containing 25, 33, or 50% glycerol were evaluated at 65°C to study the influence of *G* on the pasting properties and on the rheological behavior.

For each composition, η data were recorded over time. Tests were performed in two stages (Fig. 2). The first stage was carried out to study the characteristics of the pasting and gelatinization process; the second one, at various shear rates ($\dot{\gamma}$), was performed to determine the rheological behavior of the system after complete gelatinization. This method is useful for studying the effects of the previous shear history on the flow behavior of time-dependent fluids such as starch.[38,39] Because of the geometry of the system, $\dot{\gamma}$ was constant over the entire thickness.

In the first stage (constant $\dot{\gamma} = 20\ \mathrm{s}^{-1}$), the evolution of η over time was recorded. After complete gelatinization occurred and the starch reached its steady state or residual η, $\dot{\gamma}$ was decreased to $1\ \mathrm{s}^{-1}$, and the second stage was started.

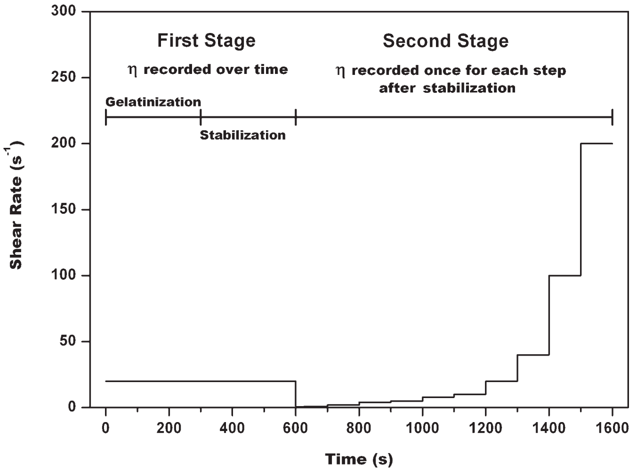


Figure 2 Scheme of $\dot{\gamma}$ versus time applied in the measurement of the pasting properties and rheological behavior of starch.

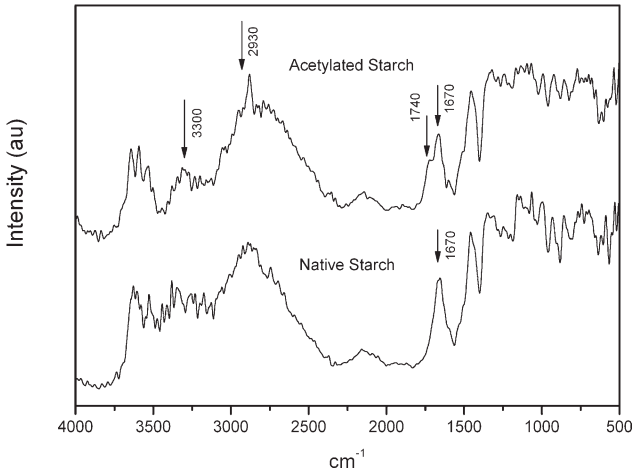


Figure 3 FTIR spectra for the native and acetylated potato starch.

In the second stage ($\dot{\gamma} = 1\text{–}200\ \mathrm{s}^{-1}$), the rotational speed was gradually increased. For each value of $\dot{\gamma}$, the η value was recorded after stabilization (1 min). The stabilization time was selected to minimize the thixotropic and thermal/shear degradation effects.[40]

Ultraviolet (UV) matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry

Native and acetylated starch samples were dispersed in water and gelatinized in excess water (0.2 mg/mL). Measurements were performed with an Ultraflex II TOF/TOF mass spectrometer (Bruker Daltonics GmbH, Bremen, Germany) equipped with a high-performance solid-state laser ($\lambda = 355$ nm) and a reflector. The system was operated with the FlexControl 2.4 software package (Bruker Daltonics GmbH, Bremen, Germany). Samples were irradiated with a laser power of 30% and were measured in the linear mode in positive and negative ion modes. The samples were loaded onto a sample plate (MTP 384 polished steel TF, Bruker Daltonics). Mass spectra were the sum of 100 single laser shots; the laser power depended on the sample. 2,5-Dihydroxybenzoic acid (DHB; i.e., gentisic acid) and norharmane (nHo) were used as matrices. Matrix stock solutions were made via the dissolution of 2 mg of DHB or nHo in 1 mL of 1 : 1 (v/v) MeCN–H_2O. Analyte–matrix deposits were prepared with the thin-film layer sandwich method.[41]

RESULTS AND DISCUSSION

FTIR characterization of the native and acetylated starches

Figure 3 shows the FTIR spectra of both native and acetylated starches. Characteristic peaks for the chemical groups present in the amylose and

TABLE II
FTIR Characteristic Peaks for the Chemical Groups Present in the Starch Structure

Bands (cm^{-1})	Assignment
3450	OH hydroxyl group
2920, 2880, 1430, 1320, 1275,1245	Symmetric or asymmetric CH$_2$ stretching vibration, attributed to the pyranose ring
1740	Carbonyl group vibration
1670	Vibrations of water molecules adsorbed in the noncrystalline region of starch
1415, 1320	Vibrations of OH, CH in the ring
1235–1457	C—O group
1150	C—O bond stretching of C—O—H
1078–1016	C—O bond stretching of —C—O—C— in the glycosidic linkage
850, 838	CH$_3$COH group the anhydroglucose ring of starch

amylopectin molecules are described in Table II. For the native granular potato starch, the band from 3200 to 3400 cm^{-1} could be observed because of the stretching of intermolecular and intramolecular bonds of starch hydroxyl groups. The peaks at 2984 and 2912 cm^{-1} were due to the formation of intermolecular and intramolecular bonds between starch and glycerol hydroxyl groups. A carbonyl stretch peak at 1740 and 1235 cm^{-1} (C—O) appeared because of the acetylation of OH from starch, and there was strong evidence of the presence of an ester group (C=O) chemically bonded to the starch. This confirmed that the acetylation treatment was performed successfully.[33]

DSC

The DSC technique was used to compare the thermal behavior of native and acetylated starches. The results are shown in Figure 4.

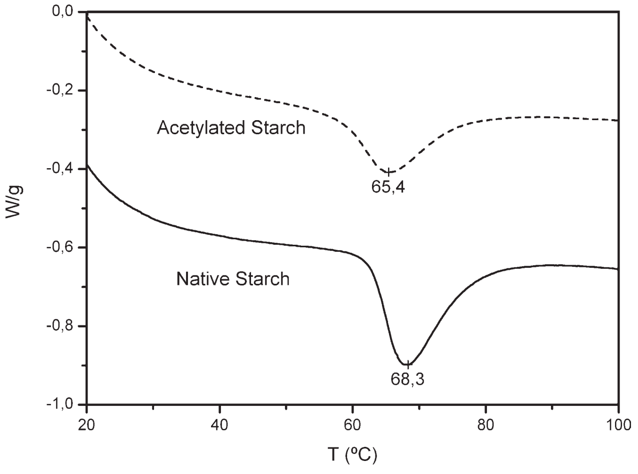


Figure 4 DSC of the native and acetylated potato starch.

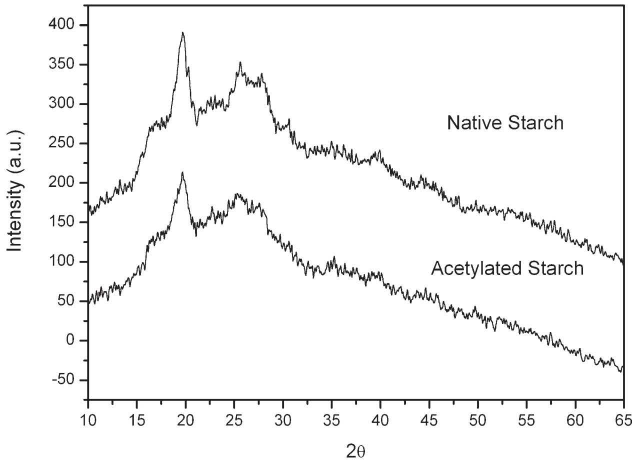


Figure 5 XRD of the native and acetylated potato starch granules.

Both thermograms showed an endothermic peak corresponding to the gelatinization of starch. Native starch showed a sharper peak at 68.3°C with an onset temperature of 61.2°C and an end-set temperature of 79.3°C. Acetylated starch showed a smaller and broader peak at 65.4°C, which started at 57.3°C and ended at 77.3°C.

The acetylation of starch produced a decrease in the gelatinization temperature (peak, onset, and end set), and this indicated that the structure of the starch granules was partially broken during the treatment. In addition, the gelatinization heat decreased from 19.3 to 13.5 J/g.

Crystallinity values of the native and acetylated starches by XRD

XRD has been used to reveal the crystalline structure of starch granules.[1–4,42] Figure 5 shows XRD of the potato starch (type B). The peak at $2\theta = 5.6°$ (not shown), two single peaks at 16.6 and 19.7°, and the double peak corresponding to 25.6 and 27.8° are characteristic of B-type crystals observed in starches from potatoes. The crystallinity values showed a slight decrease from 27% for native starch to 22% for acetylated starch. Zhang et al.[43] found similar effects and attributed the decrease in the crystallinity to a reduction in the amount of hydrogen bonds due to acetylation. These hydrogen bonds are responsible for the formation of ordered crystalline structures.

Amylose contents of the native and acetylated starches

The iodine amylose determination method showed that the amylose content in native potato starch was 29.15% ± 0.02%, and the content of amylose in acetylated starch was 27.71% ± 0.06%. Figure 6 shows

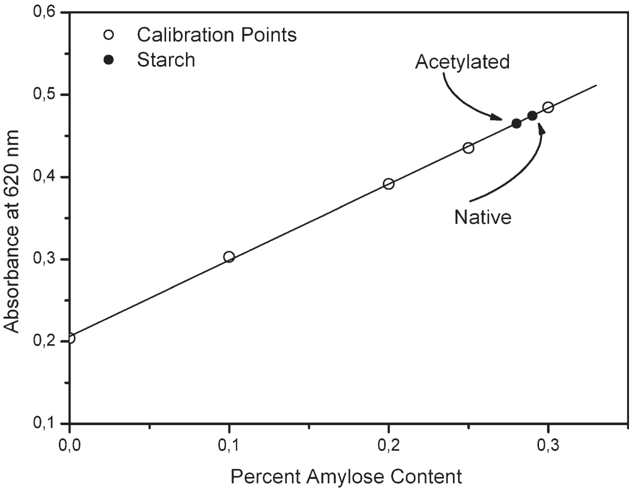


Figure 6 Determination of the amylose content.

the calibration curve and the points corresponding to native and acetylated starches.

Process of swelling–gelatinization by optical microscopy

Upon heating in excess water, starch granules swell and increase in size several times. The swelling behavior also depends on the type of starch.[44] Subsequently, amylopectin melting allows the release of amylose. Finally, the granules are completely destructurized, and a gel-like structure is formed.[45]

Potato starch was gelatinized with glycerol and water. The starch granules absorbed water, swelled, and increased in size several times. Before rupturing, the crystalline granules were observed with cross-polarized light optical microscopy [Fig. 7(a)]. After the rupture of the granules, no evidence of crystals was observed [Fig. 7(b)], and an amorphous material, usually called thermoplastic starch, was obtained.

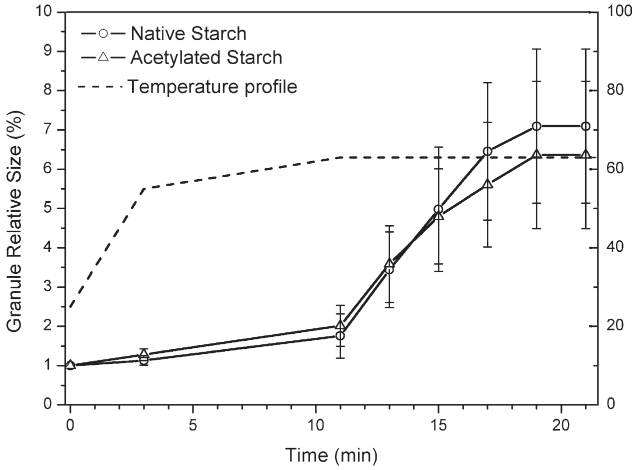


Figure 8 Swelling of the starch granules as measured by optical microscopy.

During swelling, amylose leaches from granules.[44–46] Therefore, amylose is the main component in the supernatant, whereas amylopectin remains in the granules. However, small amounts of amylose remain in granules without leaching to the continuous phase.[17]

The cross-sectional area of several potato starch granules was evaluated during the specified heating program. The results showed that the size of the native potato starch granules increased 724% ± 198%. The size of the acetylated potato starch granules increased 648% ± 188% (Fig. 8). This difference can be attributed to the differences in the amylose content.[2] Other authors have shown similar results for other starch types and chemical modifications.[47] These values depend on the concentration of the solution. The high volume of the acetyl group, together with its lower ability to adsorb water, produces a lower swelling degree.[30]

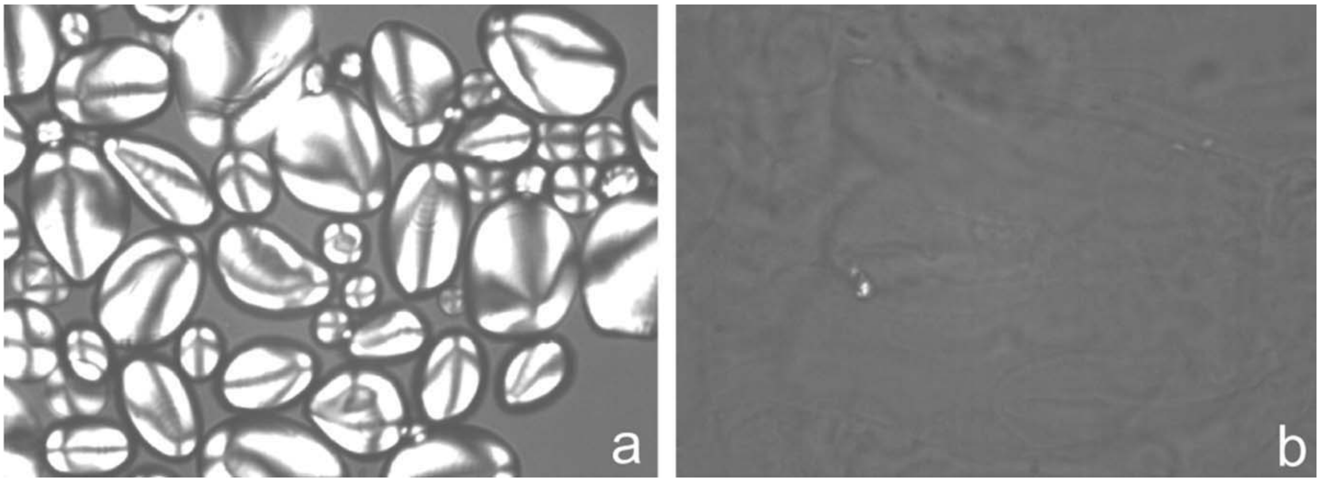


Figure 7 Optical microscopy observations in polarized light for (a) native potato starch granules before gelatinization and (b) native potato starch after gelatinization.

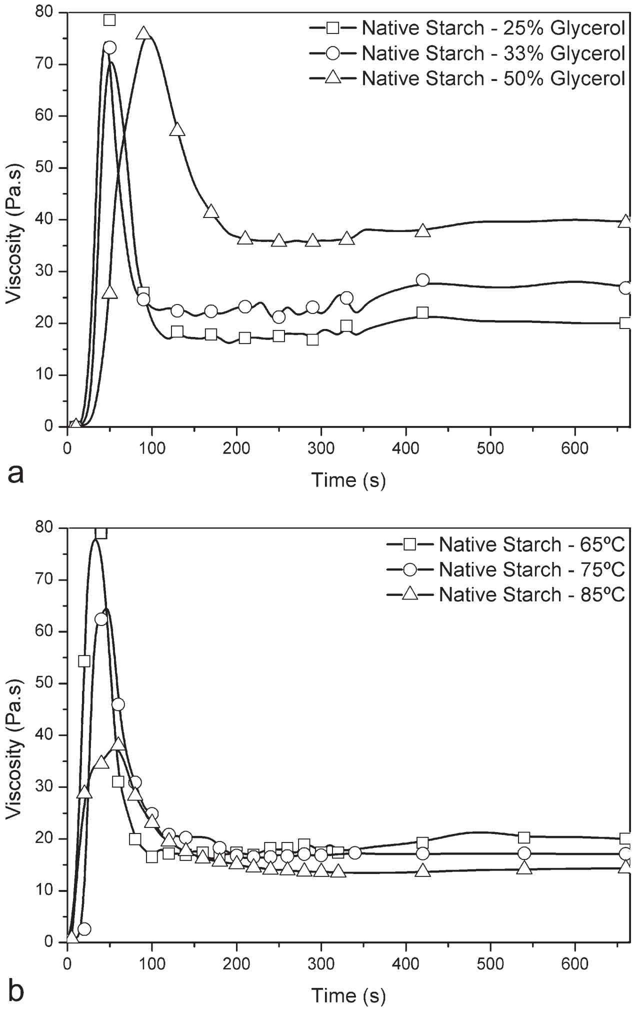


Figure 9 Starch pasting behavior depending on (a) *G* and (b) temperature.

η of starch during gelatinization

η of starch showed a rapid increase during gelatinization due to swelling. After the rupture of starch granules, a progressive breakdown in η was observed, and a constant value was reached. For native starch, that value decreased with the time of shear application, like a thixotropic fluid, until equilibrium was reached. When *G* increased from 25 to 50% [Fig. 9(a)], the η peak was wider, and the residual η value increased. This could be due to the higher η value of glycerol in comparison with water and to the formation of a complex between the glycerol and amylose molecules, which therefore modified the rheology of starch.[6] An increase in temperature resulted in smaller gelatinization peaks [Fig. 9(b)]. Moreover, the residual η value was lower at higher temperatures.

The residual η value of acetylated starch was much higher. This was caused by the presence of bulky acetyl groups, which made the alignment of starch molecules parallel to the flow direction difficult. However, this was strongly dependent on the selected value of $\dot{\gamma}$ (as shown later). When low $\dot{\gamma}$ values were imposed, the modified starch molecules had enough time to align in the flow direction. The opposite happened when high $\dot{\gamma}$ values were imposed. This effect is further discussed in the following section. Effects similar to those found for native starch were observed with respect to the influence of glycerol and temperature [Fig. 10(a,b)]. η increased with *G*, and it decreased when the temperature was increased.

Rheological behavior of the gelatinized starch

The apparent η value of starch after complete gelatinization was evaluated. Different $\dot{\gamma}$ values were imposed as explained previously. Results were fitted with two different models: the power-law model [eq. (1)] and the Ellis model [eq. (2)]. The power-law model assumes that a polymer behaves uniformly over the entire range, and the apparent η value varies as a power of $\dot{\gamma}$. It is usually used to fit high-shear regions. However, it fails to fit the low-shear

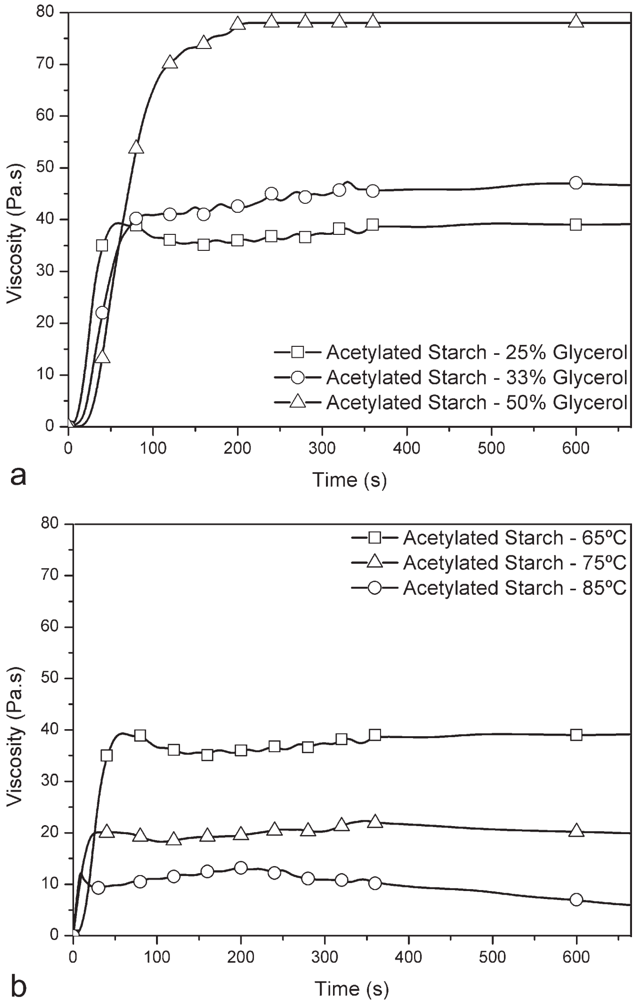
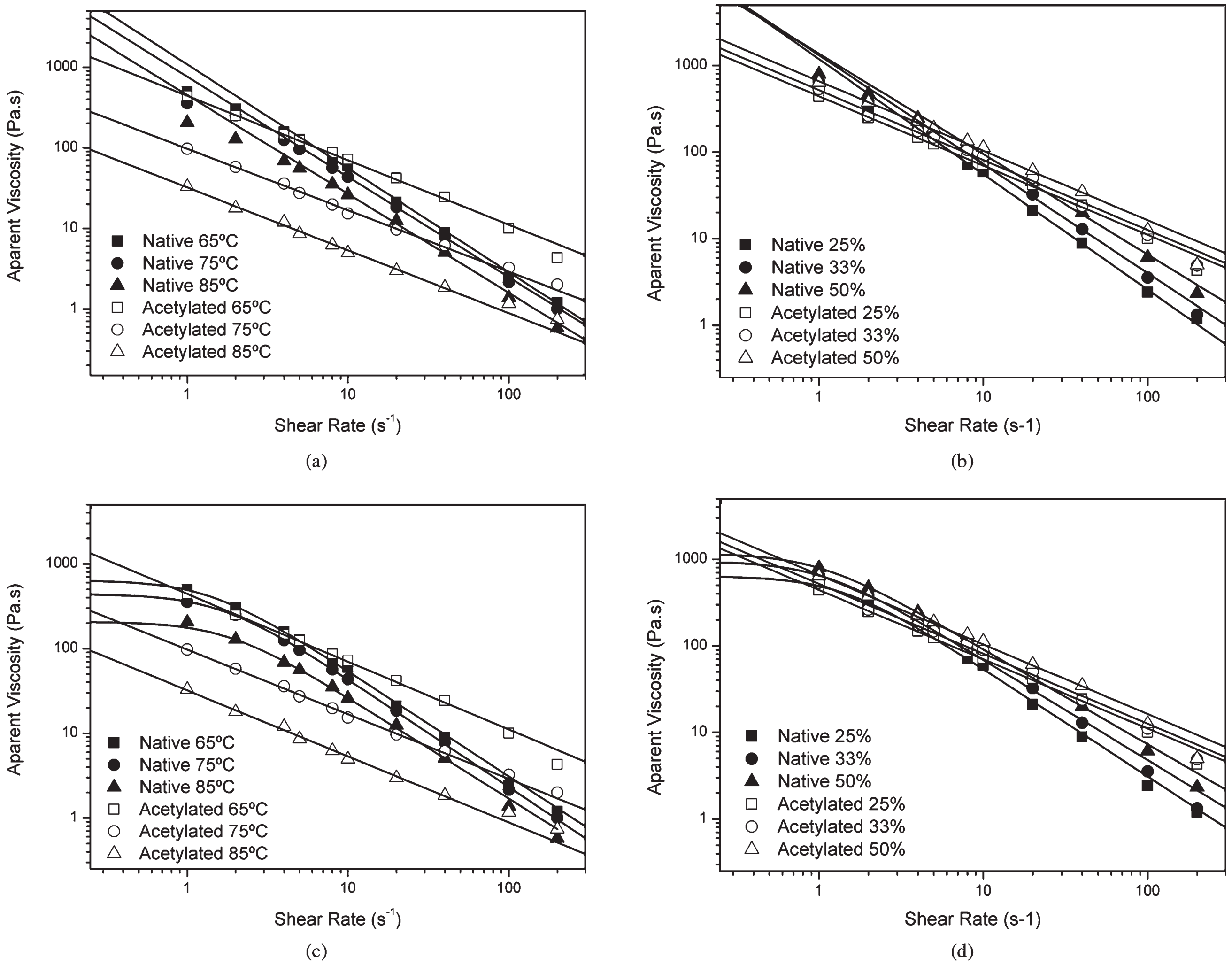


Figure 10 Acetylated starch pasting behavior depending on (a) *G* and (b) temperature.



(a) (b)

(c) (d)

Figure 11 Native and acetylated starch rheology: (a) 25% glycerol, effect of temperature, where solid lines represent power-law model fitting; (b) 65°C, effect of *G*, where the solid lines represent power-law model fitting; (c) 25% glycerol, effect of temperature, where the lines represent Ellis model fitting; and (d) 65°C, effect of *G*, where the lines represent Ellis model fitting.

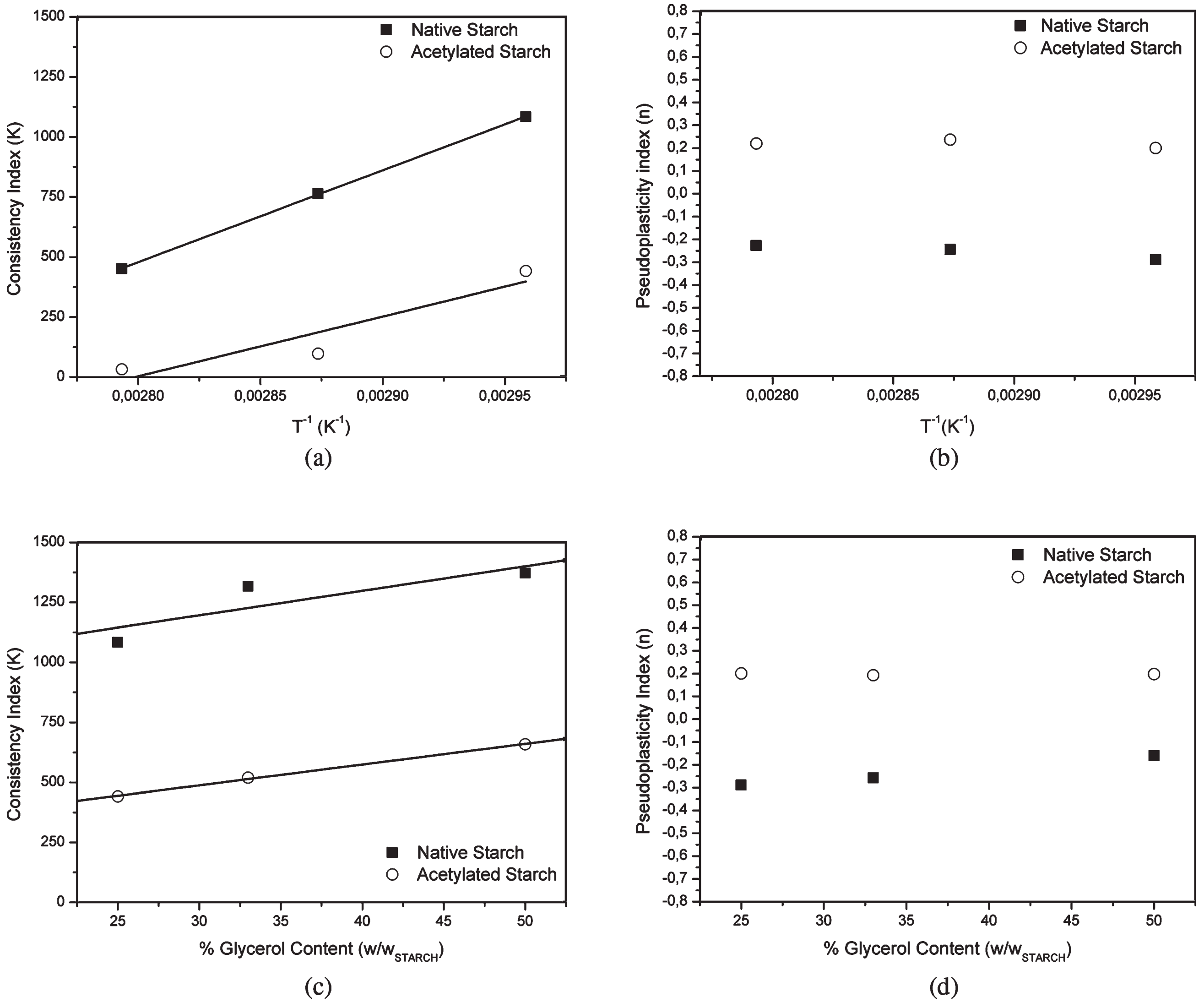
region because the prediction of η goes to infinity rather than to a constant value (as usually observed experimentally). The Ellis model predicts three zones: a Newtonian zone at low $\dot{\gamma}$ values, a transition zone at intermediate $\dot{\gamma}$ values, and a power-law zone at high $\dot{\gamma}$ values. The experimental results and the fitting curves corresponding to both models are shown in Figures 11(a–d). η of acetylated starch was lower than η of native starch for low $\dot{\gamma}$ values, and the relation was inverse for high $\dot{\gamma}$ values. This was due to the presence of bulky acetyl groups, which made the alignment of modified starch molecules in the flow direction difficult. When lower $\dot{\gamma}$ values were used, the effect of the presence of bulky acetyl groups was less important, and other factors such as the molecular weight were more relevant:

$$\text{Power-law model: } \eta = K\dot{\gamma}^{(n-1)} \tag{1}$$

$$\text{Ellis model: } \eta = \frac{\eta_0}{\left(1+\lambda^2\dot{\gamma}^2\right)^{\left(\frac{1-n}{2}\right)}} \tag{2}$$

where $\dot{\gamma}$ is the shear rate (s^{-1}), η is the viscosity (Pa s), K is the consistency index (Pa s)$^{-n}$, n is the pseudoplasticity index, η_0 represents the Newtonian viscosity (Pa s), and λ is the inflection point in the curve (s^{-1}).

The effect of temperature on the rheological behavior was studied [Fig. 11(a,b)]. For the power-law model, this factor affected the value of *K*. For the Ellis model, this factor affected the value of η_0. An increase in the temperature caused a parallel (negative) shift in the curves. In addition, acetylated starch was more dependent on temperature than native starch. In contrast, temperature had little or no effect on *n* [the curves in Fig. 11(b) are parallel to each other]. For native starch, a small increase in *n* with increasing temperature was observed in



(a) (b) (c) (d)

Figure 12 Power-law fitting parameters: (a) *K* versus temperature, (b) *n* versus temperature, (c) *K* versus *G*, and (d) *n* versus *G*.

accordance with Willet et al.[24] These results are summarized in Figure 12(a,b).

Subsequently, the effect of *G* was analyzed [Fig. 11(c,d)]. *G* had a smaller effect than temperature on η at low values of $\dot{\gamma}$, *K* (power law), and η_0 (Ellis). For higher *G* values, higher values of *K* and η_0 were observed. *n* of native starch was susceptible to changes in *G*. Greater *G* values produced less pseudoplastic behavior (lower values of *n*). This can be seen as nonparallel curves for native starch [Fig. 11(b)]. However, this effect was not found for acetylated starch, for which the plasticity index value remained almost constant, and the curves corresponding to different *G* values remained parallel. These results are summarized in Figure 12(c,d).

Aichholzer and Fritz[25] described the influence of *G* and temperature as a combined shift factor affecting *K*. They considered an Arrhenius-type dependence of *K* with temperature and glycerol [eq. (3)]. This same equation was used in this contribution. The results are summarized in Table III and clearly show the behavior mentioned previously. Fitting curves using these parameters are presented in Figure 12(a,c):

$$K = K_0 e^{\left\{\frac{1}{R}\left[(g_1+g_2 G)\left(\frac{1\;1}{T_0 T}\right)+(t_1+t_2 T)\left(\frac{1\;1}{G_0 G}\right)\right]\right\}} \quad (3)$$

where *K* is the power-law consistency index $(\mathrm{Pa\ s})^{-n}$; K_0 is the Consistency Index at the reference temperature $(\mathrm{Pa\ s})^{-\mathrm{n}}$; *G* is the percentage glycerol content (w/w); G_0

TABLE III
Combined Shift Factor Parameters

Parameter	Native starch	Acetylated starch
K_0	1116	427
G_0	0.25	0.25
T_0	338	338
g_1	−21,976	−65,936
g_2	−87,877	−263,748
t_1	−8.60	−8.25
t_2	0.03	0.03

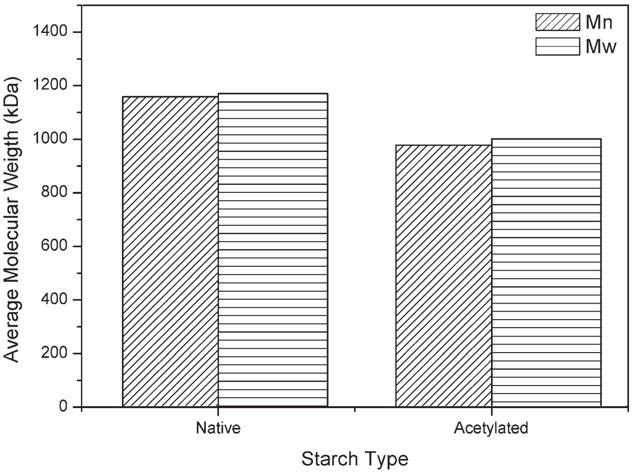


Figure 13 Average molecular weight for the native and acetylated potato starch as determined by UV–MALDI-TOF mass spectrometry (M_w = weight-average molecular weight; M_n = number-average molecular weight).

is the reference percentage glycerol content (w/w); T is the temperature (K); T_0 is the reference temperature (K); and g_1, g_2, t_1, and t_2 are fitting parameters.

UV MALDI-TOF spectrometry

The pseudoplastic behavior of macromolecules is related to the long length of the molecular chains because highly entangled structures are often more prone to shear-thinning behavior.[48] However, the less pseudoplastic behavior found for acetylated starch could be due to the partial depolymerization that may have occurred during chemical modification and thus reduced its molecular weight.[26,30]

In this contribution, the molecular weight of native and acetylated starches was evaluated. Native starch could be analyzed with both matrices (DHB or nHo) and in both modes (positive and negative ion modes). However, acetylated starch was detected only in the positive mode with the DHB matrix.

The results of UV–MALDI-TOF mass spectrometry confirmed the previous hypothesis and showed a slight decrease in the molecular weight caused by the chemical modification treatment (Fig. 13).

Many authors have investigated the effect of the acetylation of starch on its molecular weight.[30,48,49] Yadav et al.[50] demonstrated that the acetylation of starch granules reduced the molecular weight of starch. In addition, Biswas et al.[51] obtained acetylated starch and found that its molecular weight decreased when the degree of substitution increased.

CONCLUSIONS

In this contribution, native potato starch was acetylated and characterized. The influence of the chemical modification on different properties of starch was studied. The characterization included the thermal properties, crystallinity, amylose content, swelling behavior, and pasting and rheological properties. These studies are useful for the understanding and interpretation of the flow behavior of native and acetylated starches.

The chemical modification induced small changes in the crystallinity of starch. This was mainly attributed to a reduction in the number of hydrogen bonds due to acetylation. Correspondingly, a reduction in the gelatinization heat and in the range of temperatures at which it took place was observed. In addition, no significant changes in the amylose content were detected.

The swelling capacity of the granules was determined by optical microscopy with diluted solutions. The results showed that the swelling of native granules was higher than the swelling of acetylated potato starch.

The effect of acetylation was analyzed in terms of the influence of temperature and G on the pasting properties and rheological behavior of native and acetylated starches. Native and acetylated starches, with respect to their pasting behavior, responded in similar ways to changes in temperature and G.

Higher values of K were observed for native starch. The influence of temperature and glycerol on K was similar for both starch types, and it was modeled successfully with an Arrhenius dependence. A combined shift factor was used to describe the effect. Some trends were found for the plasticity index; however, more studies are required before a more general model can be proposed.

Finally, acetylated starch was found to be less pseudoplastic than native starch and presented values of the plasticity index closer to unity. This was attributed to a slight decrease in the starch molecular weight produced by chemical modification, which was confirmed by UV–MALDI mass spectrometry.

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