Chemical Modification of Cassava Starch by Transesterification Using Vegetable Oil/Aluminum Chloride

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ABSTRACT: Chemical modification of cassava starch by transesterification of a vegetable oil (palm kernel oil) using aluminum chloride as a Lewis acid catalyst was achieved under relatively mild conditions (temperature 60–110 °C; atmospheric pressure). The reaction was carried out without any additional solvent. The modified starch was characterized by degree of substitution (DS), FTIR, X-ray diffraction and thermal analysis. DS of 0.09 to 0.53 were obtained. The cassava starch presented an X-ray diffraction pattern of a type A starch. X-ray analyses showed that the reaction did not significantly affect the crystallinity of starch. The modified starch films (MStF) adsorbed less water than the reference native starch film (NStF) at all the relative humidities investigated. The MStF were also less soluble in water. The tensile tests showed an increase of the strength and a decrease of the flexibility of MStF compared to the reference NStF. The results showed that this chemical route could be used to increase the water resistance of starch-based materials.

KEYWORDS: Starch, transesterification, vegetable oil, aluminum chloride, water-resistant starch films

1   INTRODUCTION

Starch is a natural polysaccharide polymer found in seeds, roots and tubers. Starch is a renewable, inexpensive, and versatile raw material for numerous modifications (physical, thermal or chemical) [1]. Starch and its derivatives are used in various industrial applications, e.g., food, adhesives, textiles, and plastics. Modification of starch is carried out to overcome some of its main shortcomings: hydrophilic character, poor mechanical properties and dimensional instability especially in aqueous environment. One of the most important modification routes is the esterification reaction [2]. Hydroxyl groups in glucose monomer units are converted to ester moieties using acid anhydride, carboxylic acid, acyl chloride or vinyl esters, for example. Depending on the degree of substitution (DS), less hydrophilic to more hydrophobic starch soluble in organic solvents, such as acetone or chloroform, could be obtained.

Acetylation is the oldest and most widely studied starch esterification route. The acetylation of starch has been known for more than a century. Acetylated starch with almost all the possible substitution degrees from 0 to 3 can be industrially prepared nowadays using acetic anhydride or vinyl acetate in aqueous alkaline media (NaOH or KOH), acetic acid-acetic anhydride processes [2, 3]. However, acetylated starch with relatively low DS of 0.01 to 0.2 is currently of commercial interest [2]. Its use is based on the fact that it retains some properties such as film forming, binding, adhesivity, thickening, stabilizing and texturing. High DS acetylated starch has not been commercialized because of a preference for its cellulosic equivalents.

The chemical modification of starch with medium carbon-chain and long carbon- chain esters has also been studied. Santayanon and Wootthikanokkhan [4] reported that during the esterification of starch with propionic anhydride in the presence of pyridine as a catalyst, esterified starch had better stability to water. Jerachaimongkol *et al*. [5] used acyl chloride methods to fix ester chain groups from C_3–C_{18}. These authors showed that water vapor adsorption and solubility in water of the esterified starch films decreased with the length of the ester chain and the degree of substitution. Syntheses of higher fatty acid starch esters have been achieved with high DS by reaction with vinyl laurate

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or vinyl stearate using a basic catalyst such as NaOH or K_2CO_3 [6]. Gao *et al.* [7] used ionic liquids for dissolution of starch and homogeneous esterification with palmitic and stearic acids without catalysts. The modified starch obtained was more hydrophobic and more resistant to α-amylolysis. Winkler *et al.* [8] obtained fatty acid starch esters with higher DS values (DS > 2) through esterification of starch with fatty acid vinyl esters in dimethyl sulfoxide (DMSO) or with fatty acid chlorides in pyridine. Winkler *et al.* [9] also found that fatty acid starch esters with DS of 1.40–1.73 featured more starch-like product properties while fatty acid starch esters with DS of 2.2–2.63 behaved more "oil-like." As stated by Ačkar *et al.* [10], a variety of modified starch can be obtained not only by the selection of starting starch type, but also by the careful selection of modifying agents, catalysts and reaction temperature and time. However, the cost effectiveness of the various processes has to be considered for industrial applications and as competition for other products. The previous methods developed for chemical modification of the starch mentioned above used synthetic expensive chemicals and hazardous chemicals such as pyridine.

In this work, cassava starch was esterified through a new "green" approach by the direct transesterification of a vegetable oil (palm kernel oil) using aluminum chloride as a Lewis acid catalyst. Except for the aluminum chloride catalyst, the other reagents in the process were natural, renewable and low cost. Palm kernel oil is a by-product of palm oil extraction.
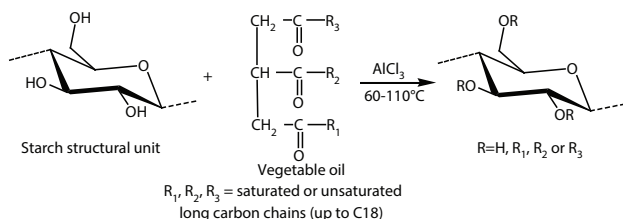
2   MATERIALS AND METHODS

2.1   Materials

Cassava starch and palm kernel oil were obtained from the local market in Yaoundé, Cameroon. The other chemicals were reagent grade and used without further purification.

2.2   Transesterification Reaction

Hydroxyl groups of starch and triglycerides of the vegetable oil were reacted according to the scheme:

Masses of starch and oil used in each experiment were defined for a stoichiometric ratio between hydroxyl groups and ester groups. The calculation was done using a chemical composition of palm kernel oil reported by Ondo [11] and the chemical composition of cassava starch (17% of amylose of molar mass 1.2×10^6 g/mol and 87% of amylopectin of molar mass 10^8 g/mol). Starch powder and the oil were pre-dried in a vacuum oven at 60°C for 24 h to remove water before each experiment.

In a typical experiment, 2 g of starch and 8.4 g of oil were weighed in a 100-mL round-bottom flask and mixed using a magnetic stirrer. Aluminum chloride (0.1 to 1% of the total mass of starch and oil) was then introduced and the mixture heated at different temperatures (60–110°C) for a defined time. The flask was fitted with a condenser and protected from humidity by a calcium chloride trap. At the end of the time period, the reaction mixture was filtered. Starch residue was washed many times with hot ethanol (95%, 50°C) to remove non-reacted oil molecules and the catalyst. Ethanol was chosen because of its ability to dissolve and extract $AlCl_3$ catalyst and in consideration of the fact that residual oil contains, in addition to triglycerides, subcomponents of fatty oils that could be formed during the experiment (diglycerides, monoglycerides, or even glycerol) that are soluble in ethanol and less in conventional hydrocarbon solvents, such as hexane, which is a well-known solvent for vegetable oil. Ethanol is not the best solvent for vegetable oils at ambient temperature. However, by increasing the temperature of the ethanol to 50°C, the solubility of oil was highly increased. Modified starch was dried in an oven at 60°C to constant mass and kept for further characterizations.

2.3   Preparation of the Films

The starch-based films were prepared by solution casting according to the method described by Qiu *et al.* [12]. In a typical experiment, 5 g of starch (native or esterified) was mixed with 93.5 g of distilled water, and 1.5 g of glycerol (30% w/w of starch) was introduced. The mixture was placed in a water bath at 90°C and mechanically stirred until the starch granules were completely gelified (viscous homogeneous mixture). The time required was about 30 min. The viscous mixture was degassed using a vacuum pump, and cast into petri disks. A constant mass of 20 g of the viscous mixture was cast into a petri disk in order to obtain films with approximately the same thickness. The mixture was dried in the vacuum oven at 60°C for 24 h. The film formed was cooled down to room temperature and kept in a petri dish for 48 h before demolding.

2.4   Characterization of Modified Starch

2.4.1   Degree of Substitution (DS)

The extent of the esterification reaction was determined by titration [4]. First, 0.5 g of modified starch was mixed with 10 mL of methanol in a 250-mL flask. Then, 10 mL of 1N NaOH aqueous solution was added for the saponification of the ester moieties. The mixture was stirred for 15 min. The excess NaOH was determined by titration with an aqueous 1N HCl solution using phenolphthalein as indicator. A blank test was carried out without starch. The percentage of substitution was calculated by the following equation [13, 14]:

$$\%Substitution = \frac{\left(V_{blank} - V_{sample}\right) \times N_{HCl} \times 0.2115}{1000 \times m_{sample}} \times 100 \quad (1)$$

where V_{blank} and V_{sample} are the volume in mL of aqueous HCl solution required for the titration of the blank and the sample respectively. N_{HCl} is the normality of the aqueous HCl solution, 211.5 the mean molecular mass of fatty ester groups of palm kernel oil and m_{sample} is the dry mass of modified starch used in the experiment.

The degree of substitution, defined as the average number of hydroxyl groups per glucose unit that have been substituted, was determined using the percent substitution according to the following equation [13, 14]:

$$DS = \frac{162 \times \%substitution}{211.50 \times 100 - \left[(211.5 - 1) \times \%substitution\right]} \quad (2)$$

where 162 is the molecular mass of a glucose unit in starch. The maximum DS value is 3, corresponding to the three hydroxyl groups present in each glucose unit.

2.4.2   FTIR

FTIR spectra were recorded between 450 and 4000 cm⁻¹ using a Bruker Alpha-P spectrometer equipped with a diamond detector.

2.4.3   X-ray Diffraction

XRD analyses were carried out on a Bruker D8 Advance Bragg-Brentano type θ-2θ° diffractometer with a Cu-Kα X-ray monochromatic radiation (λ = 1,5406 Å). The samples were analyzed over the 2θ° range of 2–70°.

2.4.4   TG-DTG

TG-DTG analyses were carried out on a Setaram SETSYS Evolution type apparatus with air flow. The temperature rise was 10°C/min. An aluminum crucible was used. A blank test was performed with the empty crucible, and the results were subtracted from the results of each sample.

2.5   Characterization of the Films

2.5.1   Water Sorption

Pieces of surface area 2 × 3 cm² size were cut from each starch-based film, dried in an oven for 24 h at 60°C, and weighed. The pieces were placed in closed desiccators containing saturated salt solutions or distilled water for different relative humidities (RH): saturated sodium chloride solution for 75% RH, saturated potassium chloride solution for 85% RH and distilled water for 100% RH. The rehydrated samples were weighed at different times to calculate the moisture content.

2.5.2   Solubility in Water

The solubility of the films in liquid water was determined according to the method presented by López et al. [15]. The 2 × 3 cm² pieces cut from the films were dried in a desiccator for 7 days. Each piece was then weighed and immersed in 80 mL of water. The mixture was stirred for 1 h at 25°C or at 100°C. Afterwards, the mixture was filtrated and the solid residue recovered and dried to constant mass in a vacuum oven at 60°C. The solubility was determined as percentage mass loss in water based on the initial mass of the dry film.

3   RESULTS AND DISCUSSION

3.1   Transesterification Reaction

The extent of the esterification reaction was determined by the measurement of the DS. Figure 1 presents the DS for reactions carried out at different temperatures with a catalyst (aluminum chloride) content of 0.1% and a reaction time of 2 h.

The results show that it is possible to esterify starch with a significant yield using a vegetable oil, such as palm kernel oil, and aluminum chloride (a Lewis acid) as a catalyst under relatively mild conditions (temperature 60–110°C, atmospheric pressure). An increase in temperature in the domain investigated increased the esterification yield, but the DS remained relatively low compared to the maximum of 3 that could be reached. The heterogeneous nature of the reaction could explain the low yield obtained. Starch retained its granular solid form during the whole reaction, so that only a part of the hydroxyl groups was accessible for the reaction, most probably those at or near the surface of each grain. Tupa et al. [16] also reported that the reactivity of hydroxyl groups in each glycose unit decreased from OH primary C(6) > OH secondary
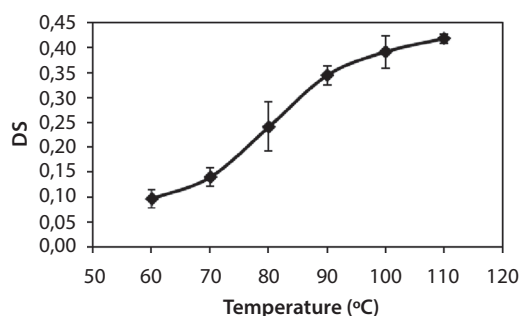
Figure 1 Reaction of cassava starch with palm kernel oil with %A1C1$_3$ = 0.1-DS as a function of reaction temperature. The results are the mean of three replicates.

Figure 2 Reaction of cassava starch with palm kernel oil at a temperature of 60°C DS as a function of catalyst concentration. The results are the mean of three replicates.

C(2) > OH secondary C(3). The secondary OH groups located at the inner part of the starch molecules form hydrogen bonds with OH in glucose units of neighboring molecules, and so are less reactive due to steric hindrance. High esterification yield is generally reported for reaction processes involving the solubilization or gelatinization of starch. Such yields are observed for acetylation using acetic anhydride or vinyl acetate in aqueous sodium hydroxide solution [3, 5, 17].

Reaction temperatures above 110°C were not tested because of the degradation of starch at this temperature. The first brown starch granules were observed at 90°C, and their proportion increased with the reaction temperature. A light brownish powder was obtained after the reaction at 110°C. Moreover, it was noted that modified starch obtained at these temperatures lost its swelling capacity in water. It was not possible to gelify the modified starch in hot water, even at temperatures of up to 120°C. We were not able to explain this behavior at this level of knowledge. Further study is necessary to understand the phenomenon.

The influence of aluminum chloride content on the reaction was also studied at 60°C. The other reaction parameters were maintained. The results are presented in Figure 2.

An increase of the DS was observed between 0.1% and 0.5%. A DS of up to 0.53 was obtained at 0.5% aluminum chloride content. At catalyst content above 0.5%, DS decreased slightly. The maximum DS obtained by increasing the catalyst content was approximately near the maximum value obtained by increasing the reaction temperature. It seems that the inaccessibility of OH groups, as mentioned earlier, is a limiting factor of the reaction.

It should be noted that DS obtained in this study are in the range of commercially esterified starches (DS 0.09–0.53) [3]. So, the esterified starch could be used in most of the current applications of commercial acetylated starch (food packaging, blend polymers,
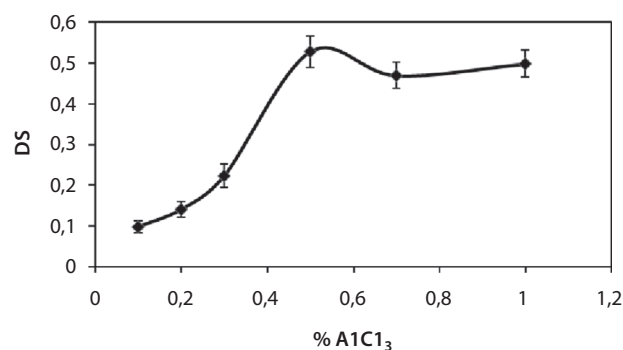
food additives). However, for applications requiring highly hydrophobic starch, high values of DS could be obtained by using pregelatinized starch as a starting material, for example. The ratio of hydroxyl groups in pregelatinized starch accessible for esterification is potentially more important than in granular starch. A study to verify this is ongoing and the results will be shown elsewhere. Esterification reaction could also be performed under homogeneous conditions using a solvent to solubilize starch. Recent works in the literature have shown that fatty acid-starch esters with high DS values could be "sustainably" produced using homogeneous processes and a recyclable solvent. Söyler and Meier [18] reported transesterification of maize starch to DS > 2 through a homogeneous process using olive oil or a high oleic sunflower oil as reactive reagent, dimethyl sulfoxide (DMSO) as recyclable solvent and 1,5,7-triazabicyclo[4,4,0]dec-5-ene as catalyst. Söyler and Meier [19] also reported a similar level of DS with another process involving diallyl carbonate as a benign reactive reagent and 1-butyl-3-methylimidazolium chloride as ionic liquid solvent without catalyst. The advantage of the procedure claimed in this work is to involve mainly natural and renewable starch and fatty oils that could be found everywhere in the world, especially in developing countries. Improvements of the procedure for the preparation of high DS products are in progress, and the results will be shown elsewhere.

3.2 Characterization of Modified Starch

Native and esterified starch were characterized by FTIR. In Figure 3, the spectrum of native starch and that of modified starch are shown.

The main vibration bands present in the spectrum of native starch were characteristic of polysaccharide materials, as reported in the literature [20, 21]. The vibration band around 3290 cm^{-1} was assigned
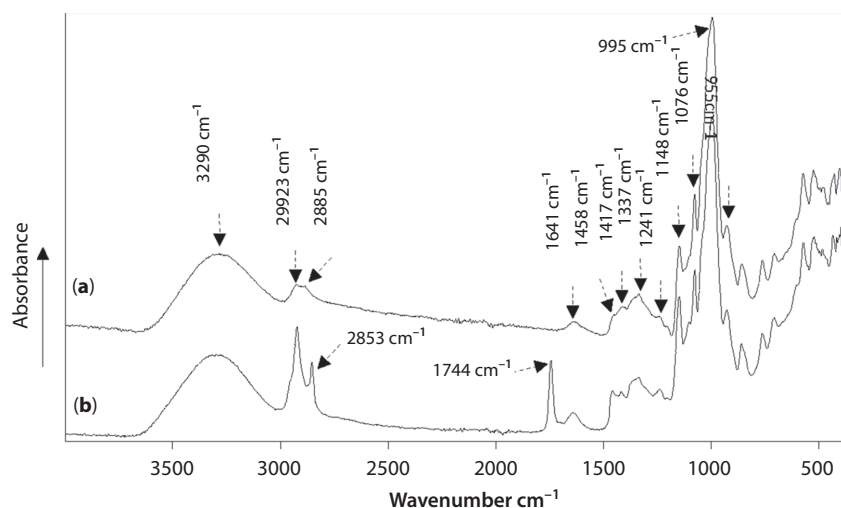
Figure 3 FTIR spectra of (**a**) native starch and (**b**) a modified starch with a DS = 0.386.
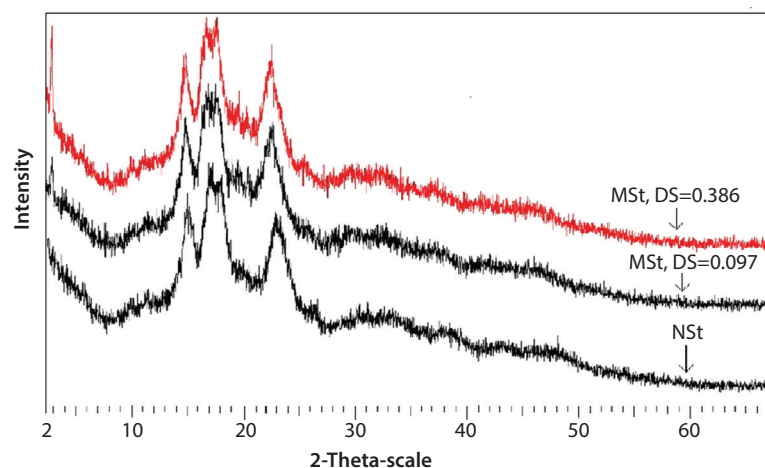

Figure 4 X-ray diffractograms of native starch (NSt), a modified starch DS = 0.097 and a modified starch DS = 0.386.

to stretching of the various OH groups in the material. The stretching of C-H bond in methylene groups was observed at 2885 cm^{-1} and 2923 cm^{-1}. The bands at 1641 cm^{-1} were attributed to bending deformation of adsorbed water in the polymer structure. The bending deformations of C-O-H, CH$_2$ appear at 1417–339 cm^{-1}. The main bands characteristic of carbon-oxygen bonds are between 1200–1000 cm^{-1}. The bands at 1148 cm^{-1} could be assigned to stretching of C-O-C groups, and the band at 1076 cm^{-1} to stretching of C-O-H groups. The stretching of C-O bonds could be seen at 995 cm^{-1}. The bands between 929–450 cm^{-1} have been attributed to the vibration of the polysaccharide backbone. The main vibration bands of native starch were found in modified starch at approximately the same position and the same intensity (except for the bands at 2886–2925 cm^{-1}), showing that the basic

chemical structure was not changed by the reaction. In addition to these main vibration bands of starch, a new band was observed at 1740 cm^{-1} in the spectra of modified starch. This band assigned to the stretching of carbonyl (C=O) of esters, confirmed the presence of ester moieties in the modified starch. An increase of the intensity of the vibration bands at 2853–2925 cm^{-1} was observed, which was probably due to the increase of the methylene (CH$_2$) and methyl CH$_3$) groups in the polymers. The ester groups in the vegetable oil are from fatty acids, i.e., they are made up of long chain alkyls composed of methylene groups and a methyl group at the end.

The influence of the reaction on the structure of starch was analyzed by X-ray diffraction. The diffractograms of native starch and modified starch are shown in Figure 4.

The X-ray diffractograms showed broad peaks at different 2θ values, i.e., 15°, 17°, 18° and 23°. Nuwamanya *et al.* [22] reported similar results, showing that these peaks are characteristic of type A starch. Cassava starch used in this work was therefore a type A starch. The diffractograms of native starch and modified starch were comparable (number and peak positions). By considering the form of the different peaks, it can be globally considered that the esterification reaction did not significantly affect the crystallinity of starch. Similar results were reported by authors for other methods of esterification [12, 16]. Qiu *et al.* [12] reported that the crystallinity of starch remained practically unchanged because modification occurred mainly in the amorphous regions.

The thermal analysis of the native starch and a modified starch was performed from room temperature to 700°C. The TG-DTG curves are shown in Figure 5.

The loss of mass of about 5% observed within the temperature range 70–130°C was due to the departure of adsorbed water. The slight increase in mass of the modified starch at the beginning of this phase was attributed to oxidation of the fatty acid ester groups. The mass reading of a TGA instrument during analysis of a fatty oil corresponds, in fact, to a combined effect of mass gain due to oxygen consumption and mass loss due to degradation [23]. Oil can gain up to 40% of its original weight during oxidation in the drying process (fixation of oxygen in the air with formation of hydroperoxides) with some weight loss due to decomposition and disappearance of volatile compounds such as aldehydes [23, 24]. This phenomenon observed in the air flow-TG of unsaturated oil, such as linseed oil, was in fact unexpected in this study given the fact that fatty acid groups in palm kernel oil

are mostly saturated. Further studies are needed to elucidate this issue. The area of active thermolysis of starch occurred between 230°C and 500°C. The curves showed two stages of degradation. The first stage was observed between 230–320°C with a maximum at 299°C and a mass loss of 55% for native starch. The corresponding maximum temperature was 288°C and the mass loss 50% for the modified starch. The second stage was observed at 398–472°C and 417–502°C for native starch and modified starch respectively. The maximum temperature was at 424°C and mass loss 32% for native starch whereas the maximum temperature was at 469°C and mass loss 40% for modified starch. The thermal degradation of starch in the first stage occurred mainly through dehydration that led to disruption of intermolecular and intramolecular hydrogen bonds of the macromolecules of starch and to depolymerization [16, 25, 26]. The relatively low mass loss and slight reduction of the maximum temperature observed in the first stage with modified starch could be due to the fact that the chemical modification reduced hydroxyl groups in starch and hence the hydrogen bonds between starch polymer chains. Several authors found that esterified starch began to decompose generally at lower temperature than native starch, but underwent a relatively low mass loss at the temperature range of 300–350°C [27]. The thermal degradation of starch in the second stage probably also involved the long carbon chain of ester groups introduced in starch. The effect of the modification on the thermal stability of starch could be more important at higher DS. The thermal degradation of native starch and of esterified starch (acetylated, butyrylated) were found to be similar at lower DS values but, at higher DS, a significant increase of the thermal stability was reported [16, 17].
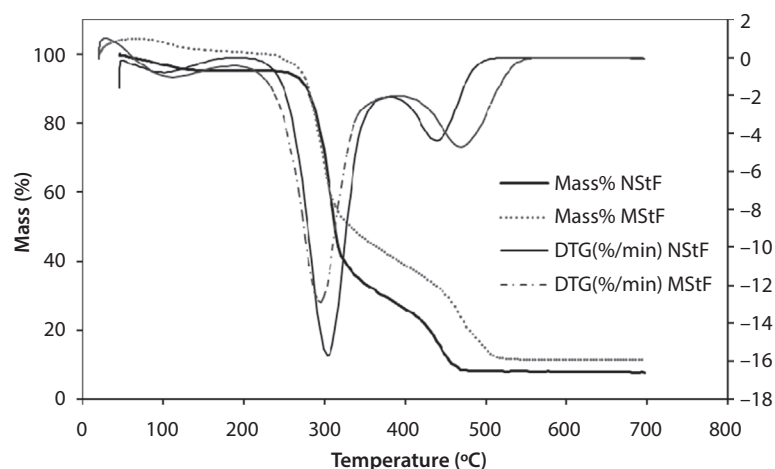

Figure 5 TG-DTG analysis of native starch (NSt) and a modified starch (MStF) with DS = 0.386.

3.3 Characterization of Starch-Based Films

3.3.1 Water Sorption

Sensitivity to water is a major drawback of starch-based plastics. Dried films of native starch (NStF) and of modified starch (MStF) were conditioned in different relative humidity environments. The percentages of water uptake as a function of time are shown in Figure 6.

The films adsorbed moisture with higher initial rates. Moisture adsorption of starch-based films also depends on the nature and the content of the plasticizer. The moisture profiles obtained are characteristic of a starch film plasticized with glycerol; glycerol, being highly hydrophilic, increases the equilibrium moisture content of the films. Similar profiles were reported by

Mali *et al.* [28]. The NStF adsorbed water up to 18%, 37% and 80% (based on their dried initial mass) after 72 h at 75%, 85% and 100% relative humid, respectively. The affinity of the films to water is due to the presence of hydrophilic hydroxyl groups in starch and plasticizer molecules that fix moisture from the surroundings through hydrogen bonds. It was observed that the replacement of some of the hydroxyl groups of starch by esters of fatty acid of a vegetable oil did not significantly affect the initial rates of water adsorption, but significantly reduced the moisture content to 12%, 28% and 67% after 72 h at the different relative humidities respectively. As expected, modified starch was more hydrophobic than the native starch. The effect on the water-resistance of the ensuing films is significant, but probably mitigated by the hydrophilic nature of the glycerol plasticizer. Important improvement of moisture resistance could be obtained by using less hydrophilic plasticizers than glycerol.

3.3.2 Solubility in Water

The solubility of starch films in water at 25°C and in water at 100°C are presented in Table 1.

The modified starch-based films showed lower solubility in water at both temperatures, confirming the reduction of the hydrophilic character of starch after the esterification. It could be noted that only modified starch with DS of 0.386, i.e., a replacement of ca.12.87% of hydroxyl groups of starch, was used for the experiment.

3.3.3 Mechanical Properties

Typical stress-strain curves of MStF and NStF are shown in Figure 7.

The tensile strength and Young's modulus obtained from the curves are reported in Table 2.

It is clear that the chemical reaction did not have a detrimental effect on the mechanical properties of the starch film. An increase of the tensile strength and Young's modulus was even observed with the MStF, showing that the film was more resistant and less flexible than the reference. The MStF was generally less
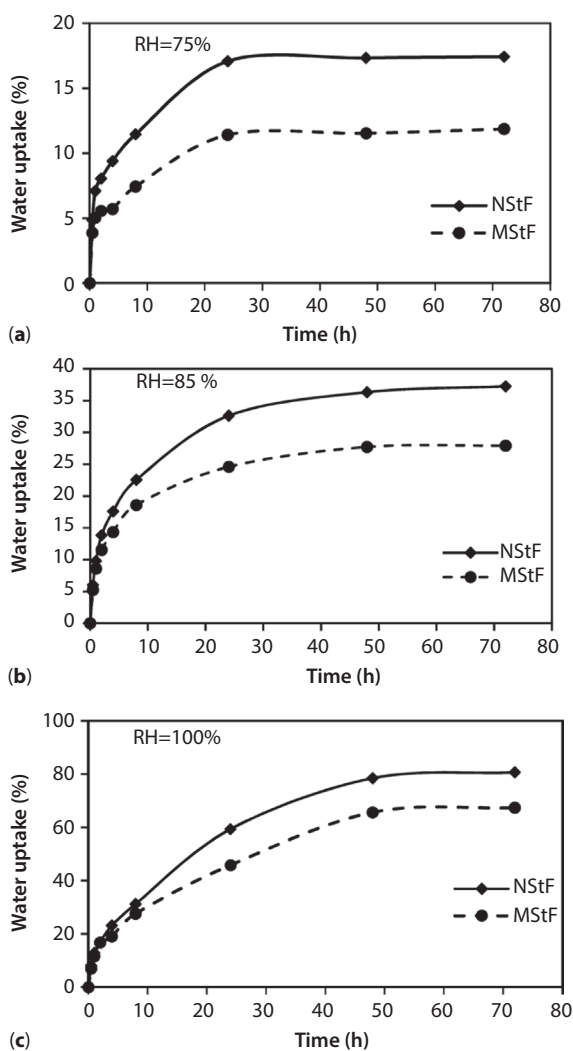

Figure 6 Water sorption of a native starch film (NStF) and a modified starch (DS = 0.386) film (MStF) at 75%, 85% and 100% relative humidity (RH). The data presented are the mean of three replicates.

Table 1 Solubility in water of native starch film (NStF) and a modified starch film (MStF) at different temperatures. The results are the mean of three replicates with the standard deviation in parentheses.

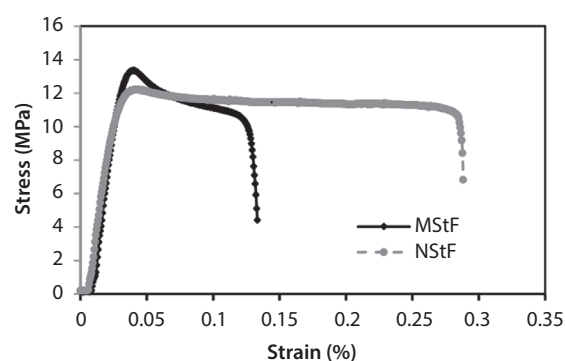| Temperature (°C)	Water Solubility (%)	
	NStF	MStF
25	31.81 (1.25)	23.55 (0.98)
100	43.27 (1.86)	31.17 (1.35)

Figure 7 Stress-strain curves of a native starch film (NStF) and a modified starch (DS = 0.386) film (MStF).

Table 2 Tensile strength of native starch film (NStF) and a modified starch DS = 0.386 film (MStF). The results are the mean of five replicates with the standard deviation in parentheses.

Sample	Young's modulus (MPa)	Tensile strength (MPa)
NStF	495 (44)	11.78 (1.49)
MStF	668 (125)	14.60 (2.99)

ductile than NStF, as shown by the curves in Figure 7. The slight increase of the resistance and decrease of the flexibility of the MStF could be due to the presence of less adsorbed water in the film. MStF adsorbed less water than NStF because of its increased hydrophobicity, as reported in the previous sections. The mechanical properties of starch-based films are affected by the plasticizer including the water adsorbed. Adsorbed water increases the plasticizing ability, and an increase of the plasticizer content decreases the mechanical resistance and increases the flexibility of the films, as reported by authors [28, 29].

4   CONCLUSION

The modification of cassava starch by a new chemical route using a vegetable oil (palm kernel oil) and aluminum chloride as a Lewis acid catalyst was studied. The reaction was carried out without a solvent at relatively moderate conditions (temperature 60–110°C, atmospheric pressure). Modified starches with degree of substitution (DS) of 0.09 to 0.53 were obtained. FTIR, X-ray diffraction and thermal analyses showed that the starch backbone and the crystallinity were not significantly changed by the reaction. Water sorption and solubility in water of the films from native starch and modified starch were compared. As expected, modified starch films (MStF) adsorbed less water than native starch films (NStF) in all the different relative

humidity environments investigated. The MStF were less soluble in water than the reference. All the results showed an increase of the hydrophobicity of starch after the modification. The mechanical properties (tensile strength and Young's modulus) of the films were not dramatically affected by the modification. An increase of the tensile strength and Young's modulus was even observed with modified starch, probably due to the low amount of adsorbed water in the films. Adsorbed water increased the plasticizing effect, and thus reduced the films' strength and increased the flexibility.

ACKNOWLEDGMENT

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