

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 C₃–C₁₈. 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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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 $70\text{--}130^\circ\text{C}$ 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 $230\text{--}320^\circ\text{C}$ 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 $398\text{--}472^\circ\text{C}$ and $417\text{--}502^\circ\text{C}$ 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 $300\text{--}350^\circ\text{C}$ [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].

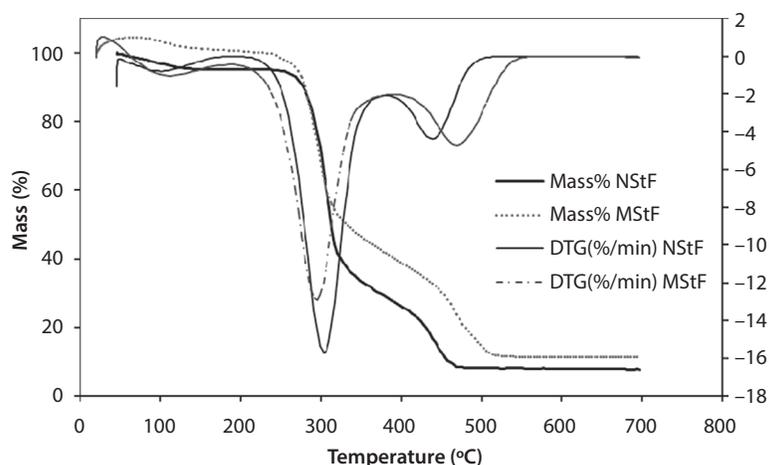


Figure 5 TG-DTG analysis of native starch (NSt) and a modified starch (MSt) with DS = 0.386.

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 humidity, 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

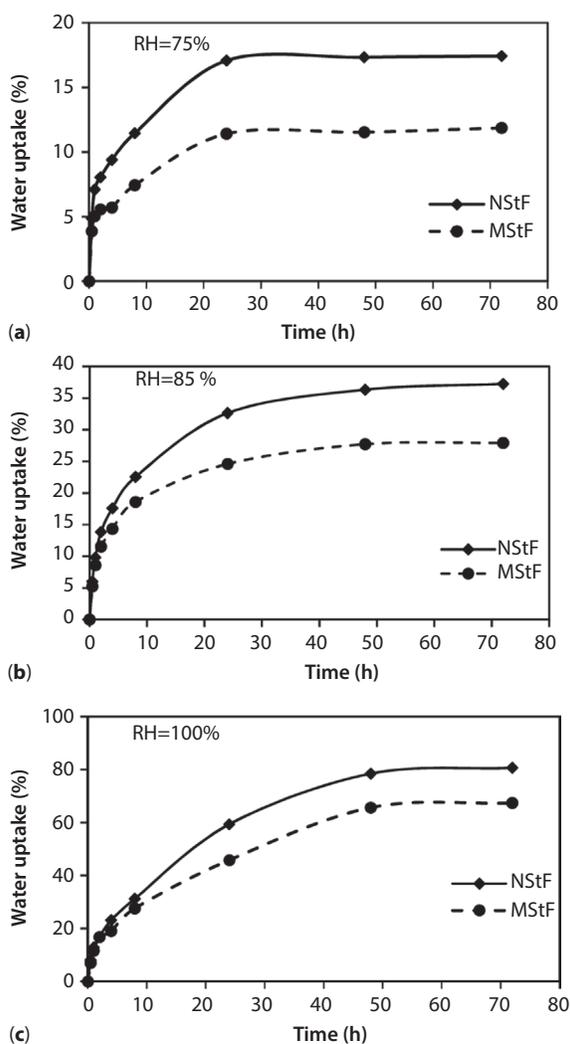


Figure 6 Water sorption of a native starch film (NStF) and a modified starch (DS = 0.386) film (MStF) at 75%, 85% and 100% relative humidity (RH). The data presented are the mean of three replicates.

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)

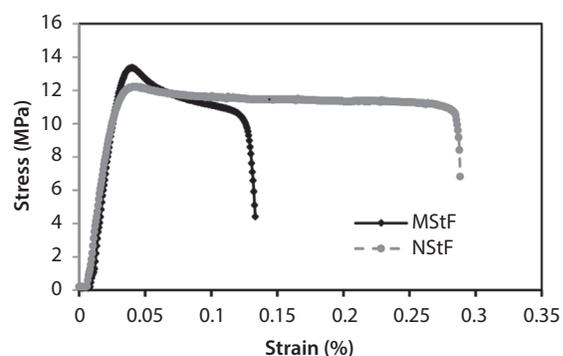


Figure 7 Stress-strain curves of a native starch film (NStF) and a modified starch (DS = 0.386) film (MStF).

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.

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REFERENCES

1. D. Schwartz and L.R. Whistler, History and future of starch, in *Starch: Chemistry and Technology*, 3rd ed., ch. 1, pp. 1–10, J. BeMiller and L.R. Whistler (Ed.), Elsevier Inc., San Diego (2009).
2. J. Hong, X.-A. Zeng, C.S. Brennan, M. Brennan, and Z. Han, Recent advances in techniques for starch esters and the applications: A review. *Foods* **5**, 50 (2016). doi: 10.3390/foods 5030050R.A. De Graaf, A. Broekroelofs, and L.P.B.M. Janssen, The acetylation of starch by reactive extrusion. *Starch/Stärke* **50**, 5, 198–205 (1998).
3. R. Santayanon and J. Wootthikanokkhan, Modification of cassava starch by using propionic anhydride and properties of the starch-blended polyester polyurethane. *Carbohydr. Polym.* **51**, 17–24 (2003).
4. S. Jerachaimongkol, V. Chonhenchob, O.Naivikul, and N. Poovarodom, Modification of cassava starch by esterification and properties of cassava starch ester films. *Kasetsart J. (Nat. Sci.)* **40**(5), 148–151 (2006).
5. L. Junistia, A.K. Sugih, R. Manurung, F. Picchioni, L.P.B.M. Janssen, and H.J. Heeres, Synthesis of higher fatty acid starch esters using vinyl laurate and stearate as reactants. *Starch/Stärke* **60**, 667–675 (2008).
6. J. Gao, Z.G. Luo, and F.X. Luo, Ionic liquids as solvents for dissolution of corn starch and homogeneous synthesis of fatty-acid starch esters without catalysts. *Carbohydr. Polym.* **89**, 1215–1221 (2012).
7. H. Winkler, W. Vorwerg, and H. Wetzel, Synthesis and properties of fatty acid starch esters. *Carbohydr. Polym.* **98**(1), 208–216 (2013).
8. H. Winkler, W. Vorwerg, and R. Rihm, Thermal and mechanical properties of fatty acid starch esters. *Carbohydr. Polym.* **102**, 920–941 (2014).
9. Đ. Ačkar, J. Babić, A. Jozinović, B. Miličević, S. Jokić, R. Miličević, M. Rajič, and D. Šubarić, Starch, modification by organic acids and their derivatives: A review. *Molecules* **20**, 19554–19570 (2015).

10. M.S.E. Ondo, Huile de palmiste traditionnelle, Doctoral thesis, Université Cheikh Anta Diop, Sénégal, pp. 57–61 (2003).
11. L. Qiu, F. Hu, and Y. Peng, Structural and mechanical characteristics of film using modified corn starch by the same two chemical processes used in different sequences. *Carbohydr. Polym.* **91**, 590–596 (2013).
12. M. Elomaa, T. Asplund, P. Soininen, R. Laatikainen, S. Peltonen, S. Hyvärinen, and A. Urtti, Determination of the degree of substitution of acetylated starch by hydrolysis, ¹H NMR and TGA/IR. *Carbohydr. Polym.* **57**, 261–267 (2004).
13. L.-F. Hong, L.-H. Cheng, C.Y. Lee, and K.K. Peh, Characterisation of physicochemical properties of propionylated corn starch and its application as stabiliser. *Food Technol. Biotechnol.* **53**(3), 278–285 (2015).
14. O. López, M. García, and N. Zaritzky, Film forming capacity of chemically modified corn starches. *Carbohydr. Polym.* **73**, 573–581 (2008).
15. M. Tupa, L. Maldonado, A. Vázquez, and M. L. Foresti, Simple organocatalytic route for the synthesis of starch esters. *Carbohydr. Polym.* **98**, 349–357 (2013).
16. Y. Xu, V. Miladinov, and M.A. Hanna, Synthesis and characterisation of starch acetates with high substitution. *Cereal chemistry*. **81**(6), 735–740 (2004).
17. Z. Söyler and M.A.R. Meier, Catalytic transesterification of starch with plant oils: A sustainable and efficient route to fatty acid starch esters. *ChemSusChem* **10**, 182–188 (2017).
18. Z. Söyler and M.A.R. Meier, Sustainable functionalization of cellulose and starch with diallylcarbonate in ionic liquids. *Green Chem.* **19**, 3899–3907 (2017).
19. M. Fan, D. Dai, and B. Huang, Fourier transform infrared spectroscopy for natural fibres, in *Fourier transform – Materials analysis*, S.M. Salih (Ed.), pp. 45–69 ISBN: 978-953-51-0594-7, InTech, Available from: <http://www.intechopen.com/books/fourier-transform-materials-analysis/fourier-transform-infrared-spectroscopy-for-natural-fibres> (2012).
20. F.J. Warren, M.J. Gidley, and B.M. Flanagan, Infrared spectroscopy as a tool to characterise starch ordered structure—a joint FTIR–ATR, NMR, XRD and DSC study. *Carbohydr. Polym.* **139**, 35–42 (2016).
21. E. Nuwamanya, Y. Baguma, N. Emmambux, and P. Rubaihayo, Crystalline and pasting properties of cassava starch are influenced by its molecular properties. *Afr. J. Food Sci.* **4**(1), 8–15 (2010).
22. P. Fjällström, B. Andersson, C. Nilsson, and K. Andersson, Drying of linseed oil paints: A laboratory study of aldehyde emissions. *Ind. Crops Prod.* **16**, 173–184 (2002).
23. Juita, B.Z. Dlugogorski, E.M. Kennedy, and J.C. Mackie, Low temperature oxidation of linseed oil: A review. *Fire Science Reviews* **1**(3) (2012).
24. E. Rudnik, G. Matuschek, N. Milanov, and A. Kettrup, Thermal stability and degradation of starch derivatives. *J. Therm. Anal. Calorim.* **85**(2), 267–270 (2006).
25. C. Beninca, I.M. Demiate, L.G. Lacerda, M.A.S. Carvalho Filho, M. Ionashiro, and E. Schnitzler, Thermal behavior of corn starch granules modified by acid treatment at 30 and 50°C. *Eletica. Química. São Paulo* **33**(3), 13–18 (2008).
26. Y. Gao, L. Wang, X. Yue, G. Xiong, W. Wu, Y. Qiao, and L. Liao, Physicochemical properties of lipase-catalyzed laurylation of corn starch. *Starch/Stärke* **66**, 450–456 (2014).
27. S. Mali, L.S. Sakanaka, F. Yamashita, and M.V.E. Grossmann, Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. *Carbohydr. Polym.* **60**(3), 283–289 (2005).
28. J. Bonilla Lagos, N.M. Vicentini, R.M.C. Dos Santos, A.M.Q.B. Bittante, and P.J.A. Sobral, Mechanical properties of cassava starch films as affected by different plasticizers and different relative humidity conditions. *Int. J. Food Studies* **4**, 116–125 (2015).