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Chemical modification of rice (*Oryza sativa*) and potato (*Solanum tuberosum*) starches by silanization with trimethoxy(methyl)silane

Modificación química del almidón de arroz (*Oryza sativa*) y papa (*Solanum tuberosum*) por silanización con Trimetoximetilsilano

A.M. Salgado-Delgado[1]*, E. Lozano-Pineda[1], R. Salgado-Delgado[1], J.P. Hernández-Uribe[2], A. Olarte-Paredes[1], M.J. Granados-Baeza[1]

[1]*División de estudios de posgrado e investigación, TecNM/Instituto Tecnológico de Zacatepec, calzada Tecnológico No. 27, C.P. 62780, Zacatepec de Hidalgo, Morelos, México.*

[2]*Instituto de Ciencias Agropecuarias, Universidad Autónoma del Estado de Hidalgo, Av. Universidad km 1, Rancho Universitario, C.P. 43600, Tulancingo de Bravo, Hidalgo, México.*

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Abstract

Rice starch of the A98 variety, with a denomination of origin of the state of Morelos, and potato starch were silanized to modify hydrophobicity and improve functional properties, providing added value to these starch sources and promoting their use in the formulation of biodegradable materials that require a degree of hydrophobicity, such as packaging materials. Fourier transform infrared spectroscopy analysis determined the presence of trimethoxy(methyl) silane in starch. Differential scanning calorimetry was used to determine the thermal properties and morphology was evaluated using scanning electron microscopy while changes in functional properties were assessed by identifying contact angle, swelling power, water absorption capacity, and oil absorption capacity. Hydrophobic silanized starches were obtained: Potato starch showed a contact angle of 132 ° and rice starch, 130 °. They exhibited changes in density and functionality; both swelling power and water absorption capacity were reduced in potato starch but increased in rice starch.

Keywords: Hydrophobic starch, hydrophobization, modified starch, A98 rice, trimethoxymethylsilane.

Resumen

Se silanizó almidón de arroz de la variedad A98 con denominación de origen del estado de Morelos, así como almidón de papa, con el fin de modificar su hidrofobicidad y mejorar sus propiedades funcionales, proporcionándole un valor agregado a estas fuentes de almidón y propiciando su uso en la formulación de diversos materiales biodegradables que requieran cierto grado de hidrofobicidad, como los materiales de embalaje. Se analizó con espectroscopia infrarroja por transformada de Fourier para determinar la presencia del Trimetoximetilsilano en el almidón. Se analizó mediante calorimetría diferencial de barrido y microscopia electrónica de barrido, así como el cambio en sus propiedades funcionales evaluando el ángulo de contacto, el factor de hinchamiento, la capacidad de absorción de agua y aceite. Se obtuvieron almidones silanizados hidrófobos; el almidón de papa presentó un ángulo de contacto de 132° y el de arroz, uno de 130°. Ambos mostraron cambios en su densidad y funcionalidad: el factor de hinchamiento y la capacidad de absorción de agua disminuyeron en el caso del almidón de papa e incrementaron en el almidón de arroz.

Palabras clave: Almidón hidrofóbico, Almidón modificado, Arróz A98, Hidrofobización, Trimetoximetilsilano.

* *Corresponding author. E-mail*: amsd_2303@hotmail.com
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1 Introduction

Starch is an abundant and widely available biopolymer, and its main function in nature is energy storage. It can be extracted from vegetable sources as tubercules, fruits, and cereals. Its characteristics and properties vary according to the botanical source it is extracted from (Chen *et al*., 2019). Therefore, several works aim to find novel and adequate uses, applications, and isolation techniques for starches with unconventional origins (Tagliapietra *et al*., 2021). Among the current uses of starch studied are its employment in functional foods with improved nutritional properties, flour substitute that provides better properties, the encapsulation of active compounds, and the formulation of biodegradable materials (Zhang *et al*., 2014; Martínez-Ortiz *et al*., 2017; Mohamad-Yazid, *et al*., 2018). In the industrial sector, starch is highly important since it plays an essential role as thickening agent, colloid, stabilizer, gelifier, water retention agent, and adhesive for several products (Sirivongpaisal, 2008).

Starch is chemically composed of two macromolecules, amylose and amylopectin, that are polysaccharides with a monomer (glucose) linked in chains with α 1, 4 glycosidic bonds and, in amylopectin, α 1, 6 branches. The glucose molecule contains three hydroxyl groups that tend to create secondary bonds with environmental humidity, providing the polysaccharide with a hydrophilic nature. This characteristic makes starch materials collapse and disintegrate when in contact with water, triggering poor moisture resistance, shorter durability, and weak mechanical properties (Qu and He, 2013; Bergel *et al*., 2018; Bergel *et al*., 2020).

Thanks to its nutrient content, rice is economically and socially important around the world. The crop is adaptable and grows worldwide, promoting the creation of thousands of varieties with different characteristics and properties (Chávez-Murillo *et al*., 2012). In Morelos, Mexico there are rice varieties with designation of origin because the cereal grown in this area has particular characteristics. One of these varieties from the state is A98, which possesses one of the largest starch contents and uneven maturation of starch granules (Carrillo-Gallardo, 2018). Among the qualities of rice starch are the small size of the granule and its polyhedric morphology, which largely affect the physicochemical and functional properties of the products created with rice. On the other hand, potato starch is extensively used in the food industry and others because of its low gelatinization temperature and low retrogradation tendency (Hoover, 2010).

In the past decades, several polysaccharides have been subjected to chemical modifications to find more ecological alternatives for different applications (López-Carrasquero *et al*., 2016). Within these polysaccharides is starch, which has been blended with other compounds and polymers as polylactic acid (PLA) and modified by functionalized silane grafting (Qu and He, 2013; El-Sabour *et al*., 2021). Silanes have been used as efficient coupling agents, and they show good affinity for hydroxyl groups at room temperature. The chemical reticulation of starch-functionalized silanes is carried out hydrolyzing an organosilane at a specific temperature and adding an alkaline hydroxide, allowing for a condensation reaction between Si-OH and C-OH (Amort *et al*., 1985; Wei *et al*., 2016).

To provide an added value to A98 rice starch from Morelos, this work proposes to study the response of starch in a process of modification by trimethoxy(methyl)silane (MTMS) grafts and compare it against potato starch modified by the same process. Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) were used to examine the modified starch. Additionally, contact angle, swelling factor (SP), water absorption capacity (WAC), and oil absorption capacity (OAC) were analyzed to promote the use of silanized starch in the production of materials with functionalized properties.

2 Materials and methods

A98 rice from the brand Soberano was used for starch isolation. Potato starch (CAS: 9005-25-8), sodium hydroxide (CAS: 1310-73-2), and MTMS (CAS: 1185-55-3) were purchased from SIGMA-ALDRICH. Potassium hydroxide (CAS: 1310-58-3) was purchased from Karal. Extra virgin olive oil from Carbonell was also used.

2.1 Rice starch isolate

Rice starch was isolated by alkaline hydrolysis (Palma-Rodríguez, 2012). Rice (500 g) was submerged in 0.1 M sodium hydroxide solution (2 L) and left under environmental conditions for 24 h. The supernatant was eliminated, and the rice was ground in

an Oster blender (model 6844-000-N01) at a moderate speed. The mixture was sieved through 50 and 100 mesh, with washings in NaOH (0.1 M) between each sieve. Then, pH was adjusted to 6.5 using 0.2 N hydrochloric acid and the mixture was sieved through a 200 mesh, with distilled water washings. The solution was left at 4 ºC for 24 h; the supernatant was eliminated, and the mix was centrifuged at 1000 rpm for 5 min in a centrifuge (model 800D). The supernatant was discarded again, and the precipitate was dried in a SHEL LAB oven (model VA1) at 40 ºC.

2.2 *Modification*

Starch silanization was carried out according to the reports in literature (Bergel *et al*., 2018) by mixing 18 mL MTMS with 300 mL distilled water on a magnetic stirrer at 50 ºC. Previously dried, 32 g starch was added, the mix was magnetically stirred until homogenization, and 2 g potassium hydroxide was slowly incorporated. The mixture was kept under magnetic stirring at 50 ºC for 4 h and then filtered; the precipitate was dried in a convection oven at 60 ºC for 24 h. Once the precipitate was dried, the modified starch was washed with 20 mL tetrahydrofuran and dried again at 60 ºC for 24 h.

2.3 *Characterization*

Native and modified rice starches were analyzed by Fourier transform infrared spectroscopy in a Perkin Palmer spectrometer, the powdered samples were placed on the spectrophotometer lens, and the analysis were performed in a wavelength interval from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1} and 16 sweeps and at room temperature (23 °C). Starch morphology was assessed using coating with gold with turbomolecular-pumped sputtering in a thin film deposition unit (model Desk V, DENTON VACUUM). Samples were then observed under a scanning electron microscope (model JSM-6010LA, JEOL) with an electron beam column, operating at 10 eV voltage acceleration in an ultra-high-vacuum. Differential scanning calorimetry was carried out in an equipment (model DSC Q2000) and a cooling unit from TA. Samples were moistened with 7 μL ultrapure water and ran using a nitrogen flow of 50 mL/min at 10 ºC/min from 40 to 150 ºC.

To evaluate the swelling factor and water absorption capacity (Ozturk *et al*., 2009), the starch (0.1 g) was weighed and submerged in 10 mL water in centrifuge tubes previously weighed. They were mixed in a vortex mixer for 30 s and heated in a water bath at 50, 60, 70, and 80 ºC for 30 min with stirring periods in the mixer. The tubes were then centrifuged at 3000 rpm for 15 min. The supernatant was decanted into Petri dishes previously dried at 105 ºC for 2 h. The weight of the precipitated gel was recorded, and the supernatant and gel were dried in an oven at 105 ºC for 24 h. The oil absorption capacity (OAC) was obtained following the same process at 60 ºC. The gels formed were weighed and the following calculations were obtained:

$$SP = \frac{\text{Gel weight}}{\text{Sample weight-Soluble solid weight}} \quad (1)$$

$$WAC = \frac{\text{Gel weight-Dry gel weight}}{\text{Sample weight}} \times 100 \quad (2)$$

$$OAC = \frac{\text{Gel weight (g)-Sample weight (g)}}{\text{Sample weight (g)}} \quad (3)$$

Furthermore, the modified starch was dispersed in various solvents to qualify the solubility changes after silanization. Using water, acetone, and toluene which have a polarity index of 10.2, 5.4, and 2.4, respectively. 0.5 mg of the samples were deposited on the solvents, shaken vigorously and left to stand for one hour to observe their behavior.

The contact angle was measured according to the standard ASTM D7334. A drop of 20 μL distilled water at 20 ºC was applied to a starch sample plate. It was photographed using a digital optical microscope. The statistical analysis of the data was carried out using Minitab 18, one-way ANOVA, and Tukey's test with 0.05 significance.

3 Results and discussion

3.1 *FTIR*

The FTIR analysis allowed to confirm the presence of functional groups characteristic of starch and MTMS grafts adhered to this polysaccharide (Figure 1) substituting the OH groups in the amylose and amylopectin chains. Figure 2A shows intense signals in the wavenumber 900-1200 cm^{-1}, which is attributed to stretching in C-O and C-C bonds. Previous works have linked these signals to starch since they are evidence of the presence of sugar monomers (Mohammadi and Moghaddas, 2020). For instance, the intensity of the peaks in the range of 1047-1022 cm^{-1} is related to the crystalline fraction of starches (Smits *et al*., 1998; Qin *et al*., 2016).

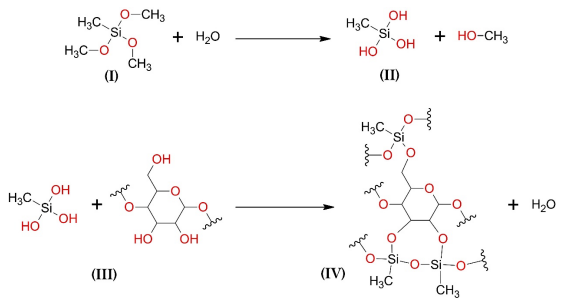

Figure 1 Proposed reaction of trimethoxy(methyl)silane (I) with water for its hydrolysis (II) and starch silanization (III) to create MTMS grafts (IV).

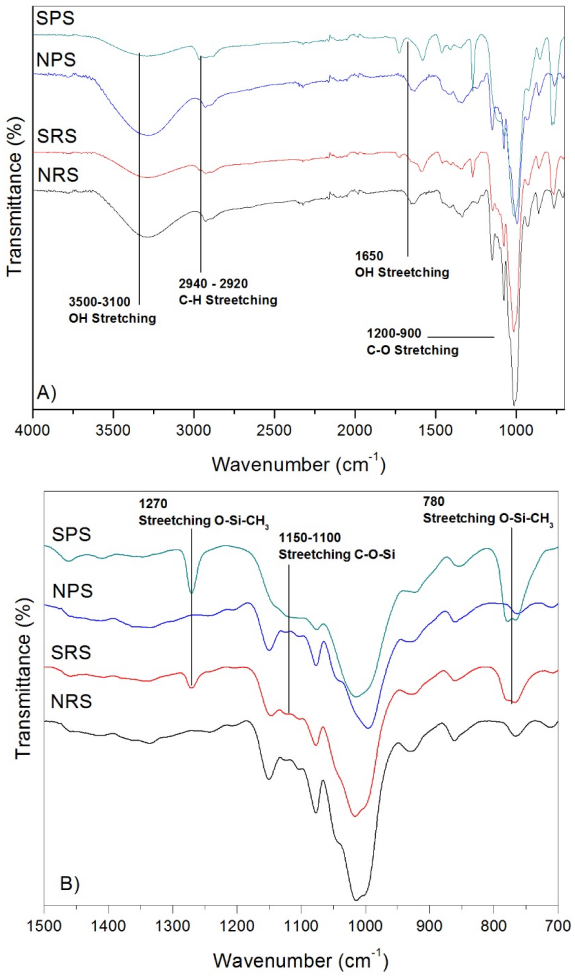

Figure 2. Infrared spectrum of native potato starch (NPS), native rice starch (NRS), modified potato starch (SPS), and modified rice starch (SRS) in the wavelength intervals a) 1000-4000 cm^{-1} and b) 700-1500 cm^{-1}.

The rice starch presented a lower percentage of transmittance in this peak, which could indicate a higher content of C-O bonds and a more crystalline organization in the starch. In addition, a band in 3300 cm^{-1} is related with -OH group stretching, mostly of those associated to hydrogen bonds reduced in modified starches. This might point to the substitution of these functional groups due to silanization and a reduction in sample moisture. A peak observed between 1700 and 1600 cm^{-1} indicates the water adsorbed by the starch samples (Gürler *et al*., 2021). Silanized starches shifted this peak to a lower wave number, representing a decrease in bond energy.

Figure 2B shows signals indicating the presence of functionalized silane used in starch modification. These peaks are found in wavelengths 1270 and 780cm^{-1}, and they are related to the vibration of the O-Si-CH_3 bond. Bergel *et al*. (2018) indicate these signals are characteristic of MTMS. In the interval 1150-1090 there is a signal related to the Si-O-C bond, attributed to the condensation reaction of the hydroxyl groups during silanization (Wei *et al*., 2016). The intensity of this signal is more noticeable in potato starch than in rice starch, likely due to a higher MTMS yield in potato starch.

3.2 DSC

The thermogram of the differential scanning calorimetry analysis for native and silanized starches (Figure 3) shows changes in crystallization temperature and the enthalpy necessary for that process. Rice showed a decrease in crystallization temperature (Tc) from 76 to 72 ºC in native and modified starches, respectively. After silanization, the Tc of potato starch increased from 66 to 69 ºC. Enthalpy was reduced in both starches, suggesting a decrease in the crystalline fraction of the starch. Bakierska *et al*. (2014) reported gelatinization temperatures of potato and rice starches of 65 and 79, respectively. These values agree with those obtained in this work. Other authors have found the change in Tc could be associated to the amylose content in starches (Mehling *et al*., 2009).

3.3 SEM

The morphology and size of the starch granules is presented in Figure 4. Rice starch granules show a smaller size than potato ones. Additionally, their polyhedric structure makes them notably different.

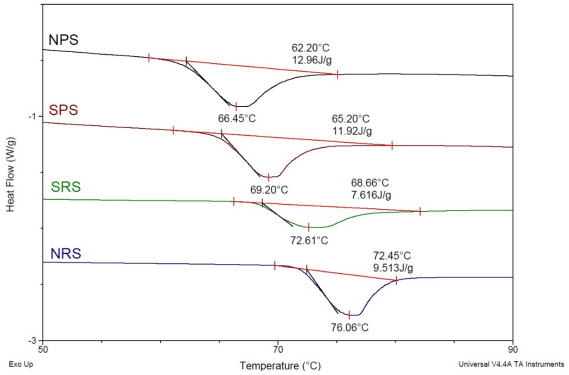

Figure 3. Comparative DSC diagrams of native and silanized potato starch (NPS and SPS) and native and silanized rice starch (NRS and SRS).

This morphology has been attributed to the competition in the maturation of the cereal, providing more rigidity to the particles that reach maturity first. In turn, they apply pressure on those that have no consolidated hard structure, resulting in irregular polyhedric shapes (Castillo *et al*., 2010). Figure 4 (b and d) shows particles adhered to the starch, creating aggregates or lumps on the granules. Because of their size, they are more noticeable on potato starch, likely because of the modification with MTMS. Wei *et al*. (2016) reports similar structures in starch nano crystals modified with hexadecyltrimethoxysilane. They observed aggregate structures and an uneven coating on the starch samples that affected their functionality. Awode *et al*. (2020) found similar lumps when modifying chitosan using trichloro(vinyl)silane. They point out that the presence of these protuberances is inversely proportional to the solubility of the material. They also reported an EDS analysis of 7.88% silicon mass.

Table 1 shows the composition of the modified starches according to the energy-dispersive X-ray spectroscopy (EDS) analysis in this work. The SRS samples analyzed presented 17.15% on silicon mass, a lower content vs that of the SPS samples (27.26%). This indicates a lower silanization in the rice starch samples that, given their polyhedric morphology and lower granule size, exhibit limited interaction with MTMS during silanization. In addition, Qu and He (2013) reported a Si content of 17.46% in samples created with a 1:1 ratio of starch and vinyltrimethoxysilane. They found that the silicon atom composition does not increase linearly with the amount of silane used because a balance is necessary for the cross linking.

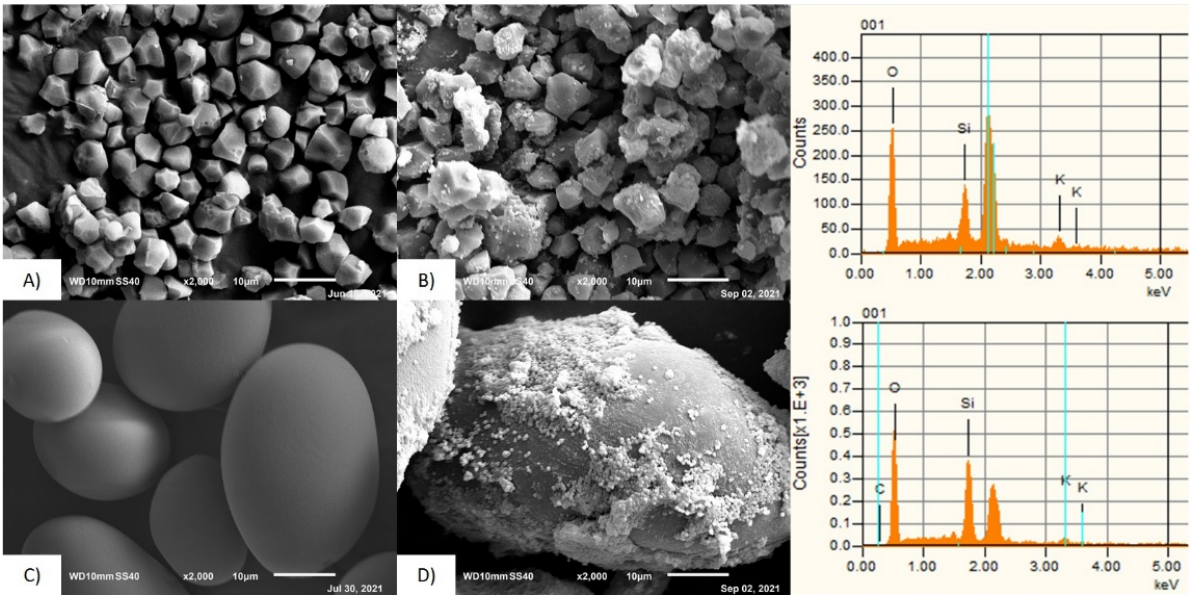

Figure 4. Micrographs of native and modified rice and potato starches (A and C; B and D, respectively) with EDS diagrams.

Table 1. Results of energy-dispersive X-ray spectroscopy analysis.

Sample	%C	%O	%Si	%K
NRS	6.89	93.11	-	-
NPS	5.48	94.52	-	-
SRS	5.16	68.74	17.15	8.94
SPS	2.33	67.02	27.26	3.39

NRS - Native Rice Starch, SRS - Silanized Rice Starch, NPS - Native Potato Starch, SPS - Silanized Potato Starch

3.4 Contact angle

The photographs taken with the optical microscope are shown in Figure 5. An average angle of 37º was measured in native rice starch while the drop was instantly absorbed in potato starch samples, so the contact angle was 0º. This proves they are highly hydrophilic materials due to the large amount of hydroxyl groups present in the amylose and amylopectin chains, allowing the formation of hydrogen bonds with water on their surface (Wei *et al*., 2016). The results of the measurements of the modified starches are found in Table 2. The SRS samples presented a contact angle of 130º and remained on the samples for 5 min, to produce a final angle of 126º. On the other hand, the SPS samples exhibited an average angle of 132º when the drop was applied and one of 128º 5 min afterwards. According to standard D7334, when the contact angle is higher than 90º, the silanized starches are hydrophobic and the wetting of these polysaccharides is reduced (Bergel *et al*., 2020). Bunkerd *et al*. (2018) obtained cassava starch modified with 2-ethylhexyl acrylate, and it presented a contact angle higher than 80º. This allowed the researchers to adhere the starch to the hydrophobic PLA matrix.

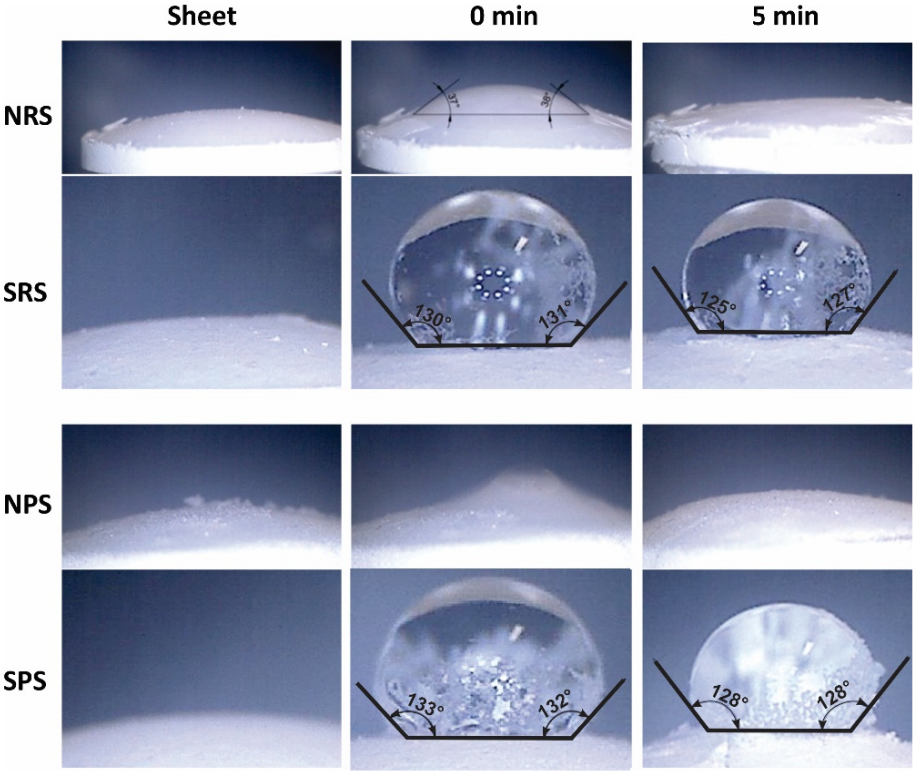

Figure 5. Photographs of distilled water drops on native rice starch (NRS), silanized rice starch (SRS), native potato starch (NPS), and silanized potato starch (SPS).

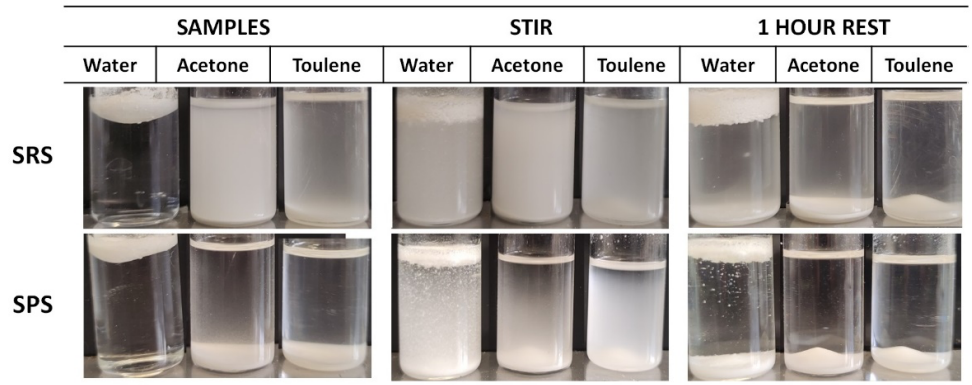

Figure 6. Solubility of modified rice and potato starches in (from left to right): water, acetone, and toluene.

Table 2. Contact angle measurements in silanized starches.

Sample	Angle (0 min)	Angle (5 min)
SRS	130 ± 1.09^{Aa}	126 ± 0.89^{Ba}
SPS	132 ± 1.86^{Ab}	128 ± 0.75^{Bb}

Means ± SD.
Means that do not share an upper-case letter between lines are significantly different.
Means that do not share a lower-case letter between columns are significantly different.

The behavior of the silanized starches against solvents with different polarity is shown in Figure 6. The water, acetone, and toluene used have a polarity index of 10.2, 5.4, and 2.4, respectively. Evidently, SRS and SPS samples precipitate in low polarity solvents (acetone and toluene), while remnants float on the water surface, which is more notable in SRS samples. This behavior indicates a density change in modified starches (Wei *et al*., 2016). Hao *et al*. (2018) observed a similar behavior in nanocrystals from potato and corn starches silanized with (3-aminopropyl) trimethoxysilane. The interaction pointed to a reduction in starch polarity and was proof of the hydrophobicity produced by the modification. They stated that the length of the carbon chains of silane affect the reduction in the polarity of nanocrystal particles. Piñeros-Guerrero *et al*., (2021), made films from the incorporation of montmorillonite clays, and polycaprolactone (PCL) to a matrix of thermoplastic cassava starch plasticized with glycerol.

Table 3. Functional properties of modified starches.

Samples	Swelling Power (g/g)			
	50 °C	60 °C	70 °C	80 °C
NRS	$3\ .18+0.38^{A}$	$3.23+0.29^{A}$	$5.87+0.55^{B}$	$9.14+0.06^{C}$
SRS	$3.52+0.18^{A}$	$5.60+1.36^{A}$	$11.04+1.66^{B}$	$10.58+0.91^{B}$
NPS	$2.16+0.32^{A}$	$10.11+0.54^{B}$	$23.04+0.35^{C}$	$37.47+0.87^{D}$
SPS	$4.14+0.35^{A}$	$5.92+0.44^{B}$	$11.54+0.41^{C}$	$11.78+0.31^{C}$
Samples	Water absortion capacity (g/g)			
	50 °C	60 °C	70 °C	80 °C
NRS	$2.11+0.36^{A}$	$2.20+0.25^{A}$	$4.67+0.50^{B}$	$7.71+0.08^{C}$
SRS	$2.35+0.24^{A}$	$4.22+1.20^{A}$	$9.08+1.44^{B}$	$8.34+0.66^{B}$
NPS	$1.05+0.30^{A}$	$8.54+0.48^{B}$	$20.12+0.36^{C}$	$32.13+0.64^{D}$
SPS	$4.14+0.41^{A}$	$5.92+0.43^{B}$	$11.54+0.38^{C}$	$11.78+0.31^{C}$

Means ± SD. Means that do not share an upper-case letter between lines are significantly different.

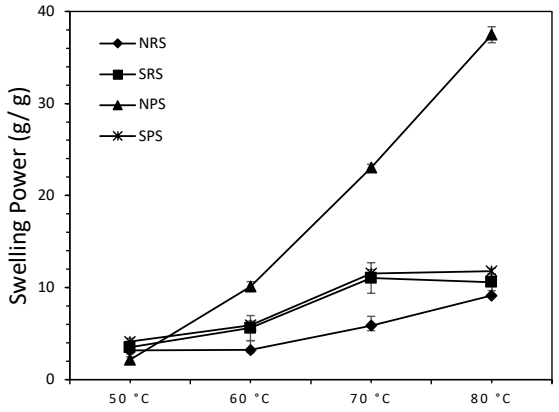

Figure 7. Graph showing the swelling factor of native rice starch (NRS), native potato starch (NPS), silanized rice starch (SRS), and silanized potato starch (SPS) at different temperatures.

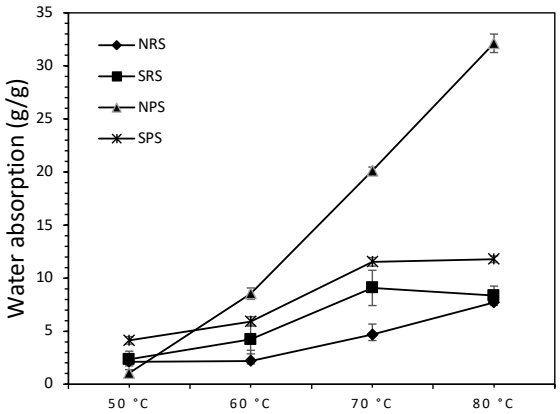

Figure 8. Graph of the water absorption capacity of native rice starch (NRS), native potato starch (NPS), silanized rice starch (SRS), and silanized potato starch (SPS) at different temperatures.

Finding that the addition of PCL reduces the solubility due to the amount of hydroxyl groups that interact with the ester groups of PCL, which hinders the interaction with water molecules. Also mentioning the importance of this factor in the production of biofilms as it influences other properties such as mechanics and barrier. Therefore, according to what was observed in this analysis, the decrease in the interaction of starches with water and a change in their polarity are notable. This could promote its permeability to water and use in various applications.

The functional properties are summarized in Table 3. The swelling factor at different temperatures is presented as a graph in Figure 7; the behavior of this property in native and modified starches is shown at different temperatures. Native potato starch exhibited a swelling factor of 37.47 g/g at 80 ºC, evidently superior to that of rice (9.14). This is due to the larger granule size that considerably increases the swelling capacity (Ali *et al*., 2016).

A swelling factor of 20.5-90 ºC has been reported for A98 rice starch (Chávez-Murillo *et al*., 2012), higher than that of other rice variants analyzed. This work presents limited swelling, likely due to the presence of amylose-lipid complexes that could affect the granular swelling capacity (Cornejo-Ramírez *et al*., 2018). Furthermore, after the modification with MTMS, the granular swelling was heavily restricted in SPS samples and was only slightly increased in rice starch. The behavior of SRS samples could be linked to the fact that the amylose-lipid complex was affected during starch modification, promoting a better swelling of rice starch.

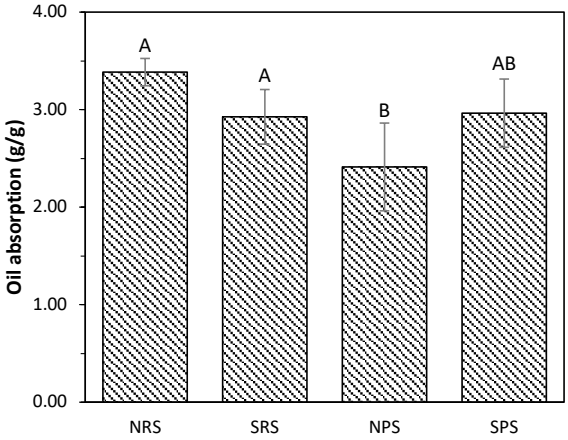

Figure 9. Bar chart of the oil absorption capacity of native rice starch (NRS), native potato starch (NPS), silanized rice starch (SRS), and silanized potato starch (SPS) at 60 ºC. The samples that share no capital letters present significant differences.

The increased SP in SRS samples is likely because the inhibition of silanized granules allows the rest to absorb larger amounts of water. This is evident in the graph shown in Figure 8 where the absorption in the SRS samples (8.56 g/g) is slightly higher than that of native starches (7.71 g/g) at 80 ºC. Gürler *et al*. (2021) observed a reduction in water solubility and absorption of PLA films created with potato starch modified with (3-aminopropyl) trimethoxysilane. They attributed this behavior to the formation of hydrogen bonds between the molecules involved, reducing the interaction between the water and the film surface. Trujillo-Ramirez *et al*. (2021)

modified rice husk using H2SO4 and NaOH as pretreatment to demonstrate its application in cell immobilization. Evaluating the water absorption rate, noting that after the treatments this factor has been reduced, which encourages the use of this agro-industrial product for the proposed application. Ashwar *et al*. (2016) evaluated the swelling of starch thermally modified and observed a significant increase in the property caused by starch gelatinization after a thermal treatment. The WAC of SPS (11.78 g/g) was significantly reduced vs that of native starch (32 g/g). These results could indicate a lower degree of modification in A98 rice starch.

The oil absorption capacity of the starches is shown in Figure 9. The SRS samples have a reduced OAC vs that of native starch, while the opposite is true for SPS samples. Still, the statistical analysis evidences these changes show no statistically significant difference. Previous works report oil absorption of 1.30 g/g in rice starch modified by phosphorylation and 0.80 in native starch at room temperature (Ashwar *et al*., 2017). On the other hand, Ali *et al*. (2016) reported OAC of 1.1 and 0.8 in starches from rice varieties and corn, respectively. According to them, this property (higher in rice starch) is relevant to food applications, where oil absorption promotes flavor retention and better feel of foods. The modification improved the lipophilic capacity of potato starch and although it seems that rice starch lost part of this property, even when in the statistical analysis there do not seem to be significant differences.

Conclusions

Modified rice and potato starches presented a high degree of hydrophobicity and changes in functional characteristics The surface area and size of granules and starch purity affect the degree of silanization. The FTIR analysis allowed to confirm the alterations in the functional groups after the modification. Furthermore, morphological changes were also observed in the micrographs obtained from the analysis in the scanning electron microscope, and a reduction was shown in the interaction with water in the potato samples. In contrast, interaction was increased in silanized rice starch, along with the swelling factor and water absorption capacity. The rice starch isolated from A98 could be potentially investigated and implemented in a number of applications; it could substitute other inorganic polymers thanks to the hydrophobicity provided by the chemical modification with trimethoxymethylsilane. The modified potato and rice starches used in this work could find their application in the obtention of thermoplastic starches, their use in biofilms, and their implementation in the creation of materials with applications in packaging systems and the production of porous materials such as aerogels

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Nomenclature

NRS	Native Rice Starch
SRS	Silanized Rice Starch
NPS	Native Potato Starch
SPS	Silanized Potato Starch
SP	Swelling Power
OAC	Oil Absorption Capacity
WAC	Water Absorption Capacity
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
DSC	Differential Scanning Calorimetry
EDS	Energy-Dispersive X-ray Spectroscopy

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