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# Structural, Physicochemical and Thermal Properties of OSA-modified Waxy Maize Starch

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**Abstract**

The aim of current work was to carry out a fine characterisation of the structural, physicochemical, and thermal properties of octenyl succinic anhydride (OSA)-modified waxy maize starch known under the marketed name Gel 'N' Melt™. Both Fourier transform infrared spectroscopy and proton nuclear magnetic resonance analyses revealed the presence of new absorption bands and confirmed the structure of OSA-modified starch in comparison with those of native starch. The results of proton nuclear magnetic resonance analysis were consistent with those obtained using the titration method. The molecular weight obtained was regarded as higher than those found for other starch modified sources; an inverse correlation between the degree of substitution and the molecular weight was deduced: a decrease in the degree of substitution was followed by an increase in the molecular weight. In addition, X-ray diffraction and scanning electron microscopy revealed the loss of the ordered A-type crystalline structure, which is characteristic of polymers with low degree of substitution. Also, a coexistence of individual and aggregate particles was observed, supported by the extent of the fusion of grains. These results were corroborated by thermal analysis experiments, which showed a total loss of the crystallinity of the heated grains.

**Keywords**

*OSA starch, Gel 'N' Melt, degree of substitution, chemical structure, molecular properties, thermal properties*

## 1 Introduction

In the modern food industry, starch presents the main component of several food formulations, and it possesses important functional properties and high nutritional value.[1] It is employed as a modifier of viscosity, adhesion, texture, and gelling agent.[2,3] However, it presents some imperfections, such as lack of fluidity, excessive viscosity, cohesive or rubbery texture (especially that derived from waxy maize), low shear, thermal resistance and high tendency towards retrogradation, which restrict its use in certain food applications.[4]

To overcome these limitations, some modification techniques have been developed in order to improve its properties, such as solubility, texture adhesion, heat capacity and tolerance, and shearing force, so as to be suitable for specific industrial applications.[5,6] These modifications also change its characteristics by limiting the retrogradation, and reducing the gelatinisation temperature. As a result, the use of modified starch improves the uniformity, stability, and texture of various foodstuffs.[7,8] One of these methods is chemical modification, which has been applied for the production of modified starch by treating native starch with octenyl succinic anhydride (OSA) to improve its functional characteristics. This modification was first patented by *Caldwell and Wurzburg*.[9] Since then, OSA starch is used in many branches of food industry, with a wide range of rheological and functional properties.[10–13]

Several researchers worked on the synthesis and properties of these macromolecules. *Guo et al.*[14] demonstrated that native potato starch could be modified by OSA with different degrees of substitution (DS). They found that the physiochemical properties of the modified polymer had improved. Therefore, the degree of substitution (DS) seems to be the principal factor responsible for various properties of the modified starch. For food applications, the values of DS ranged from 0.01 to 0.03.[15] *Huang et al.*[16] reported that the smallest chemical modification of the starches has significant consequences on their functional properties. *Han et al.*[17] investigated the relationship between the molecular structure and emulsifying properties of OSA starches with a wide range of architectures. *Zhao et al.*[13] studied the structural characterisation, and interfacial properties of three OSA starches with different multi-scale molecular structures. They observed that the DS influenced the interfacial properties of OSA starch. *Liu et al.*[18] studied the distribution of octenyl succinate groups in waxy maize starch granules. They suggested that the octenyl succinate groups are probably distributed heterogeneously in the amorphous regions throughout the whole granule. Other researchers have been interested in the rheological and thermal properties of OSA starch. *Ezzeroug et al.*[19] evaluated the properties of OSA starch using rheology and DLS. From thermo-rheological analysis, they demonstrated the presence of a thermosensitive behaviour in tangled solutions of OSA starch. These findings were confirmed by the results reported by *Punia et al.*[20] in their study on the effectiveness of heat-treated OSA-modified mungbean starches. Recently, *Wen et al.*[21] investigated the changes of pasting, gel texture, and rheological properties of modified waxy maize and five small granule starches. They found that their properties changed differentially among OSA starches. On the other hand, *Kurdziel et al.*[22] evaluated the effect of thermal treatment on structural and physicochemical properties of

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samples differing in content of octenyl succinate groups. They showed that OSA addition changed their physicochemical properties and influenced the course of physical modifications.

Although there are many studies on the physicochemical, rheological, and thermal properties of different sources of OSA starch, there are few works reported in the literature on their morphological organization combined with the structural and thermal properties. Therefore, the aim of this work was to carry out a fine characterisation of the chemical structure, morphology, and thermal properties of a commercial of OSA-modified starch, specifically Gel 'N' Melt™, which is currently used in the recent food formulations. Titration method was employed to determine the DS of modified waxy maize starch. The physicochemical and structural properties were determined using Fourier transform infrared spectroscopy, electronic scanning microscopy, molecular weight, X-ray diffraction, and proton nuclear magnetic resonance. Thermal properties were then deduced from differential scanning calorimetry and thermogravimetric analyses. The results obtained were compared with those of native waxy maize starch.

## 2 Materials and methods

### 2.1 Materials

OSA-modified waxy maize starch (Gel 'N' Melt™) was purchased from Ingredion (Manchester, UK). Waxy maize starch was purchased from IronMaxx (GmbH, Germany). The grade of both the commercial OSA-modified starch and waxy maize (WM) starch is for food and pharmaceutical uses. Chemical and reagents used were of analytical grade and commercially available. Sodium and potassium hydroxides were supplied by Fluka Chemika (USA) while ethanol, sulfuric acid, hydrochloric acid, isopropanol, acetic acid and dimethylsulfoxide (DMSO-$d_6$) were analytical reagents purchased from Sigma-Aldrich (Germany). Ultra-pure water was used for solution preparation.

### 2.2 Methods

#### *2.2.1 Preparation of stock solutions*

Stock solution was prepared by dissolving 10 g of modified starch in 100 ml of ultra-pure water at 65 °C under agitation during 30 min, and then diluted to obtain desired concentrations. The pH of prepared solutions was found equal to 5.94.

#### *2.2.2 Fourier transform infrared spectroscopy*

Chemical structures of native and modified starches were qualitatively analysed using Fourier transform infrared (FTIR) spectroscopy (Bruker, Germany). The evidence of esterification will be verified by the presence of peaks showing the shift of the hydroxyl group to the carbonyl of ester group. Native and OSA starches were dried at 105 °C for 12 h before analysis to avoid the interference from water. Samples were prepared by grinding the finely powdered starch with KBr, and scanned over a wave number range from 400 to 4000 $cm^{-1}$.

#### *2.2.3 $^1$H-NMR spectroscopy*

Proton nuclear magnetic resonance ($^1$H-NMR) was utilised to quantify the chemical structure of modified OSA maizy waize starch. $^1$H-NMR spectra was recorded on an INOVA-400 spectrometer (Varian, Palo Alto, CA, USA) operating at 400 MHz using DMSO-$d_6$ as solvent. A quantity of 0.2 g of OSA starch sample was dissolved in 1 ml of DMSO-$d_6$ at 30 °C for NMR experiment. The chemical shifts were reported in ppm.

#### *2.2.4 X-ray diffraction*

The crystallinity of OSA starch was identified by an X-ray diffractometer (D8 Advance, Bruker axs, Germany), operated at 40 mA and 40 kV, using a wavelength of 0.1542 nm monochromatic Cu-Kα radiation. The scanning scope of the diffraction angle ($2\theta$) was varied from 2 to 80° at 0.05° step size with a count time of 3 s. The modified starch samples were equilibrated at 40 °C for 24 h prior to the analysis.

#### *2.2.5 Scanning electron microscopy*

The morphology of the granules of OSA-modified starch and gelatinised OSA-modified starch was examined using a scanning electron microscopy (Jeol JSM-6400, Japan). Before testing, the samples were fixed onto metallic sample holders with conducting silver glue, and then sputtered with a layer of gold. The tension of acceleration of the electrons used was 5 kV, and detector-sample outdistances varied between 9 and 14 mm.

#### *2.2.6 Degree of substitution*

The degree of substitution (DS) is the average number of hydroxyl groups substituted per glucose unit. The DS of OSA starch was determined by titration as previously reported by *Nilsson et al.*[23] OSA starch sample (5 g, dry weight) was weighed and dispersed by stirring for 30 min in 2.5 M HCl diluted in isopropanol (25 ml). Then, 100 ml of 90 % (v/v) aqueous isopropyl alcohol solution was added, and the slurry stirred for an additional 10 min. The suspension was filtered through a glass filter, and the residue washed with 90 % isopropyl alcohol solution until no $Cl^-$ could be detected any longer (using 0.1 M $AgNO_3$ solution). The starch was re-dispersed in 300 ml of distilled water, and then the dispersion was heated up in a boiling water-bath for 20 min with stirring. The starch solution was titrated with 0.1 M standard NaOH solution using phenolphthalein as an indicator. A blank was simultaneously titrated with native starch as a control. The DS was calculated using Eq. (1).[24]

$$DS = \frac{0.162\frac{V \cdot M}{W}}{1 - 0.210\frac{V \cdot M}{W}} \quad (1)$$

$V$ is the titration volume of NaOH solution (ml), $M$ is the molarity of NaOH solution, and $W$ is the dry weight (g) of the OSA starch.

For comparison, the DS was also deduced from the results of $^1$H-NMR spectra using Eq. (2).[25]

$$DS = \frac{I_{methyl}}{3I_{anometic\ proton}} \quad (2)$$

$I_{methyl}$ is the integrated signal of the NMR peak from methyl group, and $I_{anomeric\ proton}$ is the integrated signal of the NMR peak from anomeric proton.

### *2.2.7 Viscosity-average molecular weight*

The intrinsic viscosity of a macromolecule depends on its molecular mass, structure, and polymer-solvent interactions. Measurements of intrinsic viscosity, expressed in ml g$^{-1}$, are carried out by preparing solutions with various concentrations in the DMSO solvent.

Specific viscosity ($\eta_{sp} = (t - t_0)/t_0$) and reduced viscosity ($\eta_{red} = \eta_{sp}/c$) were calculated by the determination of three parameters: time of flow of solution ($t$), time of flow of solvent ($t_0$) measured in the viscometer, and solution concentration (C) in mg ml$^{-1}$. The intrinsic viscosity was obtained by extrapolation of $\eta_{sp}/c$ to zero concentration, according to Eq. (3).

$$\eta = \lim_{C \to 0}\left(\frac{\eta_{sp}}{c}\right) \quad (3)$$

An Ubbelohde capillary viscometer (Fungilab), thermostatically controlled at 25.0 ± 0.1 °C, was used to measure the intrinsic viscosity ($\eta$) of samples at about 5.0 mg ml$^{-1}$ dissolved in DMSO. The average viscometric molecular weight ($M_w$) was estimated using Eq. (4), which gives the relation between $\eta$ and $M_w$.

$$\eta = K \cdot M_w^{\alpha} \quad (4)$$

$K$ and $\alpha$ are constants that depend on the system polymer-solvent and temperature. In our case, $K = 51.8 \cdot 10^{-3}$ and $\alpha = 0.51$.[26]

### *2.2.8 Thermal analyses*

Thermal analyses were realised using both differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), according to the method proposed by *Krueger et al.*[27]

DSC analysis was carried out using a DSC model (SDT Q600 V20.9 Build 20, TA Instruments). An amount of three mg of polymer was accurately weighed in an aluminium pan, and distilled water was added (1 : 3, w/w dry basis: water). The pans were placed in closed stainless steel DSC pans, and heated from 25 to 700 °C with a heating and cooling rate of 10 and 5 °C min$^{-1}$, respectively, in a nitrogen atmosphere with $N_2$ filled at 100 ml min$^{-1}$. The pans were hermetically sealed and allowed to stand for 2 h at room temperature before analysis. Gelatinisation temperature was determined by automatically computing gelatinisation onset temperature ($T_o$), peak temperature ($T_p$), conclusion temperature ($T_c$), and gelatinisation enthalpy ($\Delta H_{gel}$) from the endothermic thermograms on the basis of dry matter of the sample. The gelatinisation temperature range ($R$) was calculated as $2(T_p - T_o)$.[28] The glass transition temperature ($T_g$) is taken as the inflection point of the increment of special heat capacity and as the peak value of the endothermic process in the DSC curves.

TGA is a technique where a loss weight of sample can be measured as a function of time or temperature. In this study, OSA-modified starch was analysed by a thermogravimetric analyser (SDT Q600 V20.9 Build 20, TA Instruments). Sample was heated from 25 to 700 °C using open alumina crucibles.

## 3 Results and discussion

### 3.1 Molecular structures of native and OSA-modified waxy maize starches

FTIR spectra of native and OSA-modified starches are shown in Fig. 1. Both biopolymers have similar profiles. In the fingerprint region, there are several discernible absorbencies at 1148, 1078, 994, and 930 cm$^{-1}$, which were attributed to C−O band stretching.[29] The characteristic peaks at 3330 cm$^{-1}$ are the hydroxyl groups (O−H), and peaks at 2975, 2927, and 2892 cm$^{-1}$ are characteristic of C−H stretching vibration of the glucose unit, respectively. The absorption at 1641 cm$^{-1}$ is due to residual bound water. In comparison with native starch (Fig. 1, case(a)), two new absorption bands at 1740, 1693, and 1576.9 cm$^{-1}$ appeared in OSA-modified starch (Fig. 1, case (b)). The band occurring at 1740 and 1693 cm$^{-1}$ is related to C=O stretching vibration of an ester and carboxylate groups.[30] The peak at 1576.9 cm$^{-1}$ was assigned to an asymmetric stretch of vibration of a carboxyl group.[31]

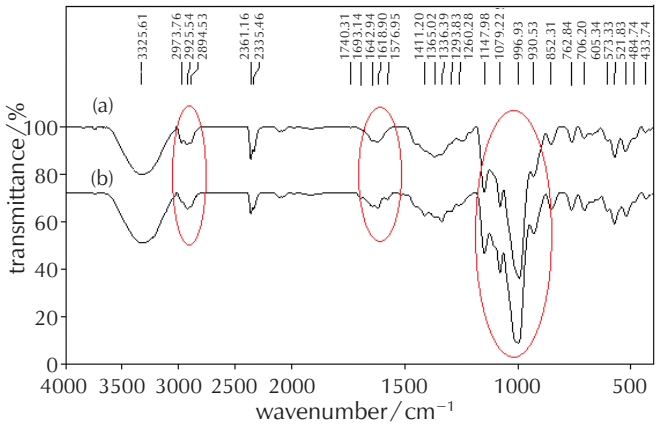



*Fig. 1* – Fourier transform infrared spectra of: (a) native starch, (b) OSA-modified starch

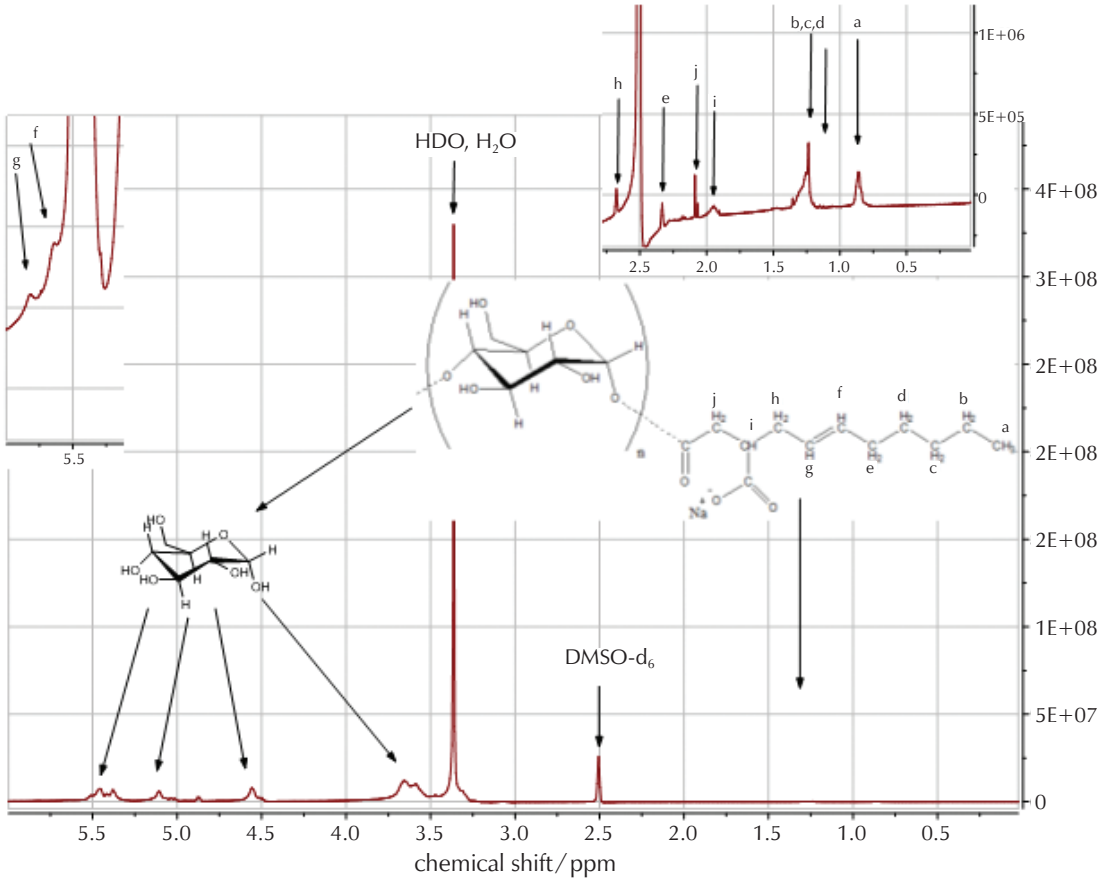



*Fig. 2* – $^1$H-NMR spectra (400 MHz, DMSO-$d_6$) of OSA-modified waxy maize starch (DS = 0.049)

In addition, the fine chemical structure of OSA-modified starch (DS = 0.049) was investigated using NMR spectroscopy. The obtained spectra presented as plots of signal intensities are shown in Fig. 2. The results obtained by $^1$H-NMR are in agreement with those found by the titration method. According to the literature,[34] the hydroxyl protons appear between 3.68 and 5.6 ppm. The peak observed at 0.85 ppm (a) was assigned to the methyl protons, and it was used to measure the presence of the octenyl succinate group. The signals observed between 1.28 and 1.35 ppm (b, c, d) were from the methylene protons of the side chains of the group OS. The signal at 1.95 ppm (i) was from the methylene protons of the octenyl succinate group. The peaks at 2.33 and 2.62 ppm came from the methylene protons, and the signal at 2.68 ppm was from succinic anhydride (e, h). The peak at 5.10 ppm was from the starch equatorial proton. There was a multiplet at 5.54 ppm, and a shoulder with multiple peaks around 5.40 ppm. It had a byte with 5.82 ppm, and a shoulder with several peaks around 5.72 ppm that came from the protons of the double bond in the octenyl succinate group. The results of $^1$H-NMR and FTIR confirmed the structure of the OSA-modified waxy maize starch (DS = 0.049).

### 3.2 Crystalline structure

In order to study the effect of OSA modification on the crystalline structure, native starch, OSA-modified starch, and OSA-modified gelatinised starch (temperature of gelatinisation of 65 °C) were examined by powder X-ray diffraction analysis. Majority of the peaks (Fig. 3) were in the range of 14°–24°, indicating that the modification of waxy maize starch with OSA had no significant effect on the crystallinity of both starches under study.

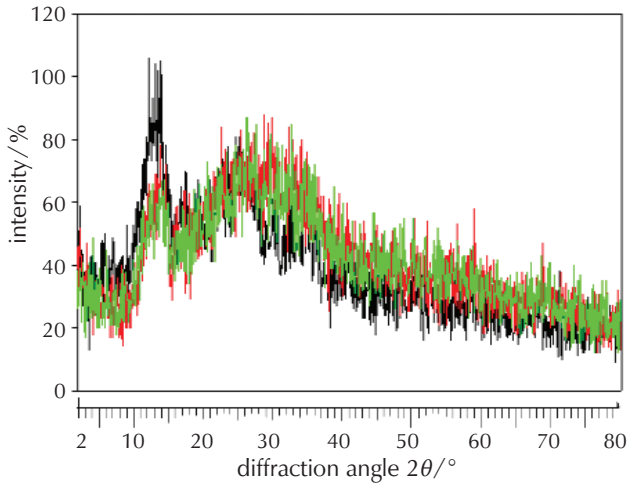



*Fig. 3* – X-ray diffraction curves of native waxy maize starch (—), OSA-modified waxy maize starch ($T_g$ = 65 °C) (—), and OSA-modified waxy maize gelatinised starch (DS = 0.0490) (—)

Fig. 3 also indicated that both studied starches showed typical A-type diffraction pattern with strong reflection at 15, 17, 18, 19, 22, and 23°. The intensity of peaks at the $2\theta$ values of 15°, 17°, 18°, and 19° were strong, whereas the peaks at the $2\theta$ values of 22° and 23° had low intensity, which was characteristic of A-type crystalline structure. This result suggested that esterification and the temperature of gelatinisation ($T_g$ = 65 °C) had not changed the crystalline pattern of samples up to DS = 0.049, although the granules of OSA-modified starches had been damaged to some extent by the modification processes. These results are in agreement with those obtained by *Wang* and *Wang*,[32] who indicated that the esterification occurred primarily in the amorphous regions, and did not change the crystalline pattern of starches in lower DS. However, this was checked by analysis in diffraction of X-rays that the crystalline types of waxy maize native starch, OSA-modified starch and gelatinised starch were preserved.

### 3.3 Molecular weight

Intrinsic viscosity describes an average molecular state of the sample. It is a sensitive indicator of the de-polymerisation of the macromolecules. Thus, all reduction in this parameter translated a decrease in average molecular mass.[32] The intrinsic viscosity of a polymer solution can be influenced by the behaviour of modified starch granules during the flow, depending on their shape and size, including the structural distribution of amylose and amylopectin.[1] The intrinsic viscosity value of modified OSA starch was 54.80 ml g$^{-1}$ ($DS_{titration}$ = 0.05). This result was regarded as suitable compared to those found for other modified starch sources, such as corn starch and oxalate starch half-ester, where the intrinsic viscosities were about 56.06 ml g$^{-1}$ (DS = 0.08), 41.34 ml g$^{-1}$ (DS = 0.4) and 22.56 ml g$^{-1}$ (DS = 0.87), respectively.[33] The estimated molecular weight of modified starch of waxy maize source (DS = 0.049) showed a somewhat higher $M_w$ ($0.847 \cdot 10^6$ g mol$^{-1}$). This result was regarded as higher than those found for other modified starch sources such as corn starch and oxalate starch half-ester, where the $M_w$ was about $1.06 \cdot 10^5$ g mol$^{-1}$ (DS = 0.08), $0.71 \cdot 10^5$ g mol$^{-1}$ (DS = 0.40), and $0.32 \cdot 10^5$ g mol$^{-1}$ (DS = 0.87), respectively, and $8.60 \cdot 10^6$ g mol$^{-1}$ (DS = 0.021) for OSA-modified starch.[34] These results demonstrated the existence of a relationship between the DS and $M_w$ of the polymer. Therefore, an increase in $M_w$ of OSA-modified starch was correlated with a decrease in DS. The reason may have been that the modification caused rupturing of some or all of the modified starch molecules.[33] Moreover, a certain degree of depolymerisation, which must have occurred during the substitution process, might also have contributed to the variation (reduction) in $M_w$.

It arises from the results of $^1$H-NMR and titration method, that the values of DS do not differ significantly ($DS_{^1H\text{-}NMR}$ = 0.049) from one another ($DS_{titration}$ = 0.050). All things considered, the DS is strongly influenced by the conditions of esterification and the botanical origin of starch.[34] OSA is adapted for the starch of waxy maize because it confers a DS of 0.052, where standards require a DS lower than 0.2 for starches intended for a food use.[15] Generally, a commercial modified starch has a DS ranging between 0.01 and 0.05.[1]

### 3.4 Morphological properties

The diversity of size of the starch granules is an important criterion for industry;[35] it predicts a certain diversity of industrial applications for the OSA-modified waxy maize starch, in particular in food industry. The SEM micrographs of samples are presented in Figs. 4 and 5, respectively. The obtained images revealed a population of particles made up of starch granules with large and small sizes. The small round grains have diameters of the order of μm, and mainly the form of polyhedric grains approximately 10–20 μm in diameter. Certain grains present a central cavity of regular form. These differences observed are related to the botanical origin and the species used. In addition, a depression of the polyhedric grains was observed, which occurred on the level of their faces. This depression is probably accentuated in the drying of structures during gelatinisation, which could be compared to a fusion on the surface of the granule of OSA-modified starch.

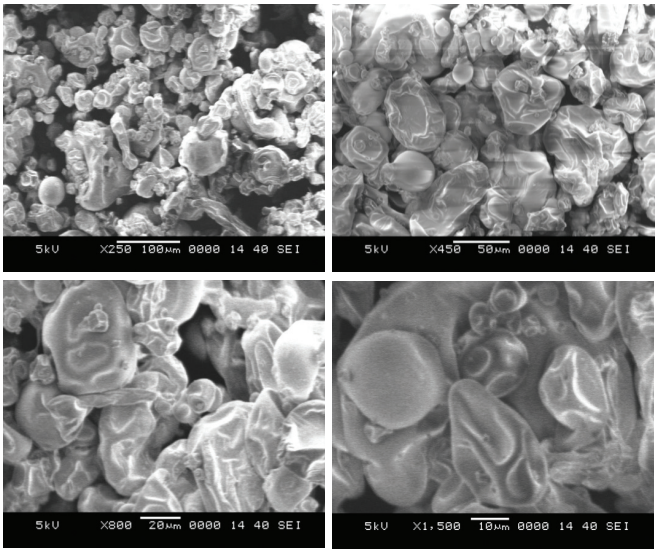



*Fig. 4* – SEM micrographs of OSA-modified waxy maize starch

According to *Herrera-Gómez et al.*,[36] the regular form is specific to the non-gelatinised granules while the irregular form indicates that the granules are gelatinised. Indeed, the heating effect (Fig. 5) causes a morphological modification of samples. On the other hand, the coexistence of individual particles with aggregate ones was observed, supported by the extent of the fusion of the grains during heating. These aggregates are made of particle clusters. The predominance of agglomerated particles of various sizes completely fragmented with less significant cavities was also observed.

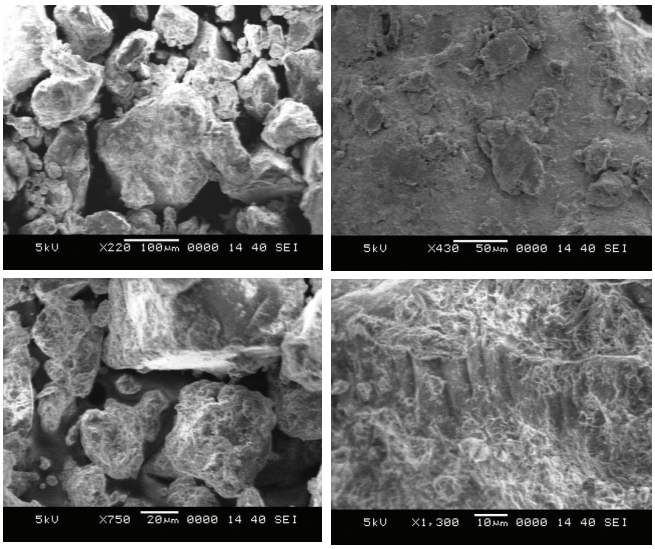



*Fig. 5* – SEM micrographs of OSA-modified waxy maize gelatinised starch ($T_g$ = 65 °C)

### 3.5 Thermal properties

DSC was used to determine the thermal parameters, such as the temperature of vitreous transition, which is described as a specific point. It is characterised by critical temperatures such as the yield temperature ($T_0$), which corresponds to the initial temperature of gelatinisation, peak temperature ($T_p$), which is the optimal temperature to obtain the yield possible gel, and the temperature of end of gelatinisation ($T_c$), as well as the heat flow of gelatinisation of the biopolymer. The thermal behaviour of OSA-modified starch reveals two endothermic peaks (Fig. 6). Initially, the slightly hydrated amorphous phase would destabilize a part of the crystalline system, causing the cooperative fusion of some crystallites.

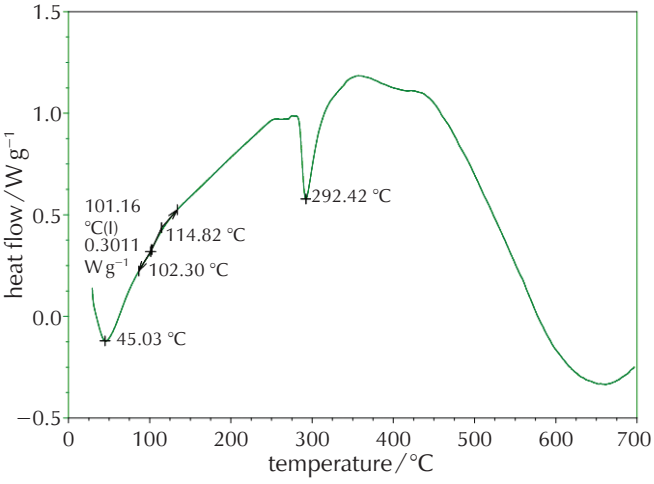



*Fig. 6* – DSC curve of OSA-modified waxy maize starch

The first endothermic peak at 45.03 °C is due to the evaporation of water related to the macromolecular chains of the biopolymer. The gelatinisation temperature ($T_g$) is the temperature at which the forces binding of amylose and amylopectin are slackened to allow molecular movements on a large scale.[37] This behaviour depends on the botanical species and possibly on the genotype (waxy corn, normal corn, corn rich in amylose). According to the literature, the $T_g$ of the native waxy maize starch is evaluated at 285 °C.[40] Gelatinisation onset ($T_o$), peak ($T_p$), and final ($T_f$) temperatures were found equal to 101.16, 102.30, and 114.82 °C, respectively, for OSA-modified starch granules. The heat flow for the sample was 0.3011 W g$^{-1}$. The gelatinisation temperature range ($R$) was 2.28 °C for a DS value of 0.050. The values of the heat flow and gelatinisation transition temperature correspond to the energy provided to dissolve the samples and to achieve gelatinisation. This means that the high transition temperatures are related to the high degree of crystallinity, which creates structural stability and makes the granule more resistant to gelatinisation.[1]

The carboxyl group repulsion effect also helped OSA starch to swell at lower temperature. Consequently, the OSA effect on the gelatinisation temperature of starch is dependent on the starch base and the value of DS. The gelatinisation enthalpy also decreases as the DS increases, indicating that modified starch granules require less energy to melt.[34] The second endothermic peak observed in DSC profile corresponded to the decomposition of the polysaccharide, which was accompanied by a release of heat at 292.42 °C. The gelatinisation properties differed from one type of sample to another. This may have been due to several factors, such as starch granule shape and size, mineral composition, and molecular architecture of the crystalline region of starch.

TGA and DTGA curves of OSA-modified starch sample (DS = 0.049) are shown in Fig. 7. The TGA curves of the studied polymer showed three typical stages of weight loss. The first phase ranging from 36.02 to 126.67 °C was attributed to the dehydration, with a weight loss of 8.32 % corresponding to a small endothermic peak in the DTGA curve for each sample, followed by a light thermal stability until 186.23 °C. After stability, two phases of weight loss were observed. The second phase corresponded to the decomposition (decarboxylation) of the organic matter in

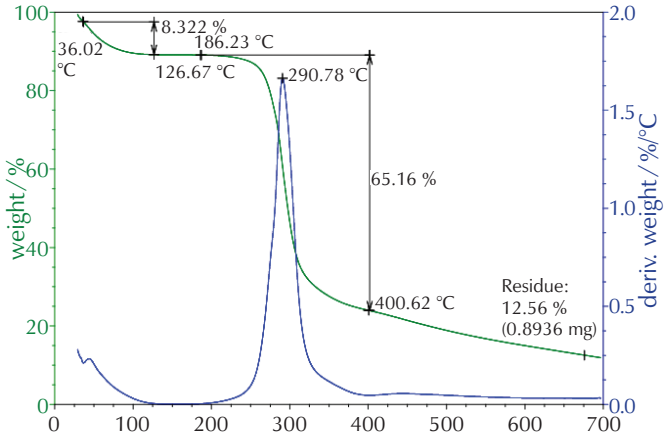



*Fig. 7* – TGA-DTGA curves of OSA-modified waxy maize starch

temperature ranges between 186.23 and 400.62 °C, with a maximum rate of mass loss of 65.16 %, corresponding to a length endothermic peak in the DTGA curve. The third phase of loss weight that exceeded 400.62 °C led to the formation of final residue of 0.8936 mg with 12.56 % weight loss. These results reveal the thermal characteristics of OSA-modified waxy maize starch. According to the temperature interval of degradation obtained for other sources of starch, the main phase of decomposition is between 290 and 350 °C.[1] The results obtained by TGA-DTGA agree well with those obtained by DSC.

The improvement in the thermal stability induced leads to a reduction in the mobility of the chains thus leading to the increase in $T_g$. According to the literature,[38] the $T_g$ at low temperatures can be allotted to the poor phase of the polymer, and the $T_g$ at high temperatures can be allotted to the rich phase, constituted mainly of amylopectin.

## 4 Conclusion

Relations between the structural parameters, morphological, and thermal properties of OSA waxy maize starch were investigated. From FTIR and $^1$H-NMR analyses, noticed was the presence of new absorption band groups, indicating that the signal intensities are lower as the DS is lower. In addition, the results of $^1$H-NMR were in accordance with those deduced from the titration method. The values of $M_w$ were found in accordance with those obtained for other sources of starch and for the same value of DS. X-ray diffraction and SEM analyses revealed a loss of crystalline structure, which is characteristic of polymers with lower DS. The coexistence of individual and aggregate particles was also observed, supported by the extent of the fusion of the grains during heating. These results were corroborated by thermal analyses, which showed a total loss of crystallinity of the heated grains. These findings can be considered as paramount elements to adapt in the polymer compositions for industrial uses.

ACKNOWLEDGEMENTS

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## SAŽETAK

### Strukturna, fizikalno-kemijska i termička svojstva voštanog kukuruznog škroba modificiranog octenil sukcinil anhidridom

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Ovaj rad imao je za cilj provesti detaljnu karakterizaciju strukturnih, fizikalno-kemijskih i termičkih svojstava voštanog kukuruznog škroba modificiranog octenil sukcinil anhidridom (OSA), poznatog pod tržišnim imenom Gel 'N' Melt™. Analize infracrvenom spektroskopijom s Fourierovom transformacijom i protonskom nuklearnom magnetskom rezonancijom otkrile su prisutnost novih apsorpcijskih vrpci s obzirom na izvorni škrob. Rezultati dobiveni protonskom nuklearnom magnetskom rezonancijom bili su u skladu s rezultatima dobivenim titracijom. Uočena je viša molekulska masa nego kod modificiranog škroba dobivenog iz drugih izvora. Utvrđeno je da postoji inverzna korelacija između stupnja supstitucije i molekulske mase: smanjenjem stupnja supstitucije dolazi do povećanja mase. Osim toga, rendgenska difrakcijska analiza i skenirajuća elektronska mikroskopija otkrili su gubitak uređene kristalne strukture tipa A, što je karakteristično za polimere s niskim DS vrijednostima. Također, uočena je koegzistencija pojedinačnih i združenih čestica. Rezultati su potvrđeni toplinskom analizom koja je pokazala potpuni gubitak kristalnosti zagrijanih zrna.

**Ključne riječi**
*OSA škrob*, *Gel 'N' Melt*, *stupanj supstitucije*, *kemijska struktura*, *molekulska svojstva*, *toplinska svojstva*

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