# Development of Maleated Starches Using an Internal Mixer

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**Summary**: Novel maleated starches (MSt) were prepared by chemical modification of cornstarch with maleic anhydride (MA), using an internal mixer as a reactor. Benzoyl peroxide (BPO) was chosen as initiator. Physico-chemical parameters were given by the process, recorded at different MA contents, under the same reaction conditions. Processing was carried out at 50 °C, 30 rpm for 8 min. Torque developed during processing was given by the digital display of the rheometer, and the total specific mechanical energy (SME) input was estimated. FTIR measurements confirmed the successful incorporation of MA into the starch backbone. X-ray diffractograms obtained for the products revealed disruption of the crystalline structure of native starch. The results indicated that the MA content had a significant effect on the characteristics of the resulting modified starches.

**Keywords:** infrared spectroscopy; renewable resources; starch; synthesis; torque rheometer

## Introduction

Starch and chemically-modified starches have been used extensively. Their applications vary from biodegradable packaging to components of drilling muds, thickeners and gelling agents.[1] In general, modified polysaccharides have also been used as polymeric surfactants. Chemical modification of starch by partial or total esterification of its hydroxyl groups is known to reduce hydrophilicity.[2,3] Starch esters with low to high degrees of substitution (DS) may find applications as substitutes for petroleum-based plastic materials, especially in the packaging industry. However, the market penetration of such products has been low because of the relatively high production costs of starch esters.[4] Several studies have been performed in an attempt to prepare starch esters more rapidly and by environmentally friendly methods.[2,4–6]

The most applied hydrophobization methods are based on the classical esterification reaction with acyl chlorides. As an attempt to substitute the environmentally unfriendly and toxic acyl chloride process, esterification methods using mixed anhydrides were developed.[7] Several non-ionic starch esters result from reactions of starch with open-chain anhydrides, whereas the reactions of starch with cyclic anhydrides basically result in basically ionic starch esters carrying carboxylate groups.[8] Earlier transesterification reactions with fatty acid methyl esters were reinvestigated and modified for solvent-free conditions.[9] Modification of starch with alkenyl succinic anhydrides has been of interest because this modification disrupts hydrogen bonding between starch molecules and reduces starch retrogradation, while imparting an amphiphilic character.[10] These modified starches were reported to act as compatibilizers in PE/starch blends. However, reactions were performed adding octenyl succinic anhydride (OSA) in starch/water slurries, which requires long drying periods to recover the product.[11]

Interestingly, cyclic dibasic acid anhydrides, such as maleic anhydride (MA), can

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yield starch esters containing a free carboxylic acid group, which is able to promote acid-catalyzed transesterification reactions with biodegradable polyesters, leading to the formation of a graft copolymer.[12] Starch maleate is an anionic material that has been used as film-forming agent for coating seeds, as superabsorbent polymers, as adhesive for the paper industry, and as drug carrier.[13] Starch maleate can be prepared by acylation of starch with maleic anhydride in aqueous base[14] or organic solvents, such as pyridine, KOAc/LiCl/dimethylformamide or NaOAc/dimethylformamide. Reactions in organic media have been performed by Paschall and Katzbeck in 1959.[15] Solvent-free reactions have also been performed by Kovats.[16] Maleation of AOT (Aerosol OT, bis(2-ethylhexyl)sodium suflosuccinate)-coated starch nanoparticles has been conducted using Novozym435 as catalyst in dry toluene.[17] These reactions typically require hours for completion and yield low DS products. U.S. Pat. N° 5,789,570 describes the solid-phase synthesis of starch maleate. According to this invention, the starch esters are products with DS between 0.2 and 2.0. They can be used as absorption material with applications in agriculture and pharmaceutical products.[8] Recently, there has been increased interest in microwave heating as a method to facilitate difficult reactions.[13] A microwave-assisted method using dimethyl sulfoxide as solvent was recently developed to prepare starch maleates with DS up to 0.25.[18] The reaction efficiency was only 50%. However, in conventional methods, a large volume of solvent has to be used, with serious environmental pollution.

Surface chemical modification is another promising method to reduce the surface hydrophilic character without changing starch bulk composition and properties. The superficial hydroxyl groups of starch can be substituted with hydrophobic groups or react with cross-linking agents to form starch networks, so that the surfaces of starch products become less sensitive to moisture. In addition, the amount of reagents used for surface modifications would be significantly lower than those in a bulk modification.[3] This procedure is in accordance with the principles of green chemistry, which also recommends the elimination of toxic organic solvents, and the reduction of energy consumption in organic syntheses. Extruders have been used as chemical reactors for polymerization reactions and for grafting hydrophobic moieties onto starch. Extruders have also been used to manufacture carboxymethylated and cationic potato starch, starch phosphates, anionic starches (esters of various dicarboxylic acids) and oxidized starches.[6]

In this study, an internal mixer was used to investigate the chemical modification of starch in the presence of maleic anhydride. The effect of MA content on the physicochemical parameters of the products was studied by FTIR and wide angle X-ray diffraction (XRD).

## Experimental Part

### Materials

Cornstarch with a moisture content of 12.7% was supplied by Corn Products Brazil (São Paulo, Brazil). Maleic anhydride (MA) and benzoyl peroxide (BPO) were purchased from Vetec Química Fina Ltda. (Rio de Janeiro, RJ, Brazil) and were used as received.

### Processing of Maleated Starch

Processing of maleated starch was carried out at a constant speed of 30 rpm for 8 min in a RheoDrive 7 internal mixer equipped with counter-rotating roller type rotors, in line with a Polylab Open System torque rheometer (Thermo Fisher Scientific, Karlsruhe, Germany). Torque during processing was obtained from the digital display of the rheometer. The processing temperature was kept at 50 °C. The maleic anhydride content was varied in the range of 0–20%, with a fixed concentration of initiator of 10%, based on the amount of added anhydride. The variation of torque

 

and temperature as a function of processing time was recorded throughout each batch. The mass of sample used in the experiments was calculated according to Equation (1). The tests were performed with 60% of the equipment capacity.

$$M(g) = [(\rho_{starch}\ X_{starch})]V_n \times 0.6 \quad (1)$$

where the density of corn starch ($\rho_{starch}$) is 1.2 g/cm$^3$ and the free volume of the equipment ($V_n$) is 69 cm$^3$.

#### Specific Mechanical Energy

The specific mechanical energy (SME) is defined as the total input of mechanical energy per unit of dry weight of processed material. It was estimated using Equation (2).[19]

$$SME = \frac{2\pi N}{m}\int_0^t C(t)dt \quad (2)$$

where N is the rotor speed (rpm), m the sample total weight (g), t the time of processing (min), and C(t) is the torque produced in time t (Nm). SME is given in kJ/kg.

#### Infrared Absorption Spectroscopy (FTIR)

FTIR spectra were recorded from 600 cm$^{-1}$ to 4000 cm$^{-1}$, using a Excalibur Series spectrophotometer, model 3100 (Varian Inc., Palo Alto, CA, USA), with an accumulation of 100 scans, and a resolution of 4 cm$^{-1}$. KBr, permanently maintained in an oven at 50 °C, was used to prepare transparent disks. The samples were extensively dried, and carefully weighed (2 mg) before grinding with KBr.

#### X-ray Diffraction (XRD)

X-ray diffraction analyses were performed with a Miniflex wide angle X-ray (XRD) diffractometer (Rigaku Corporation, Japan) operated at 30 kV, 15 mA with a nickel filtered Cu Kα radiation (wavelength = 1.542 Å). Data were acquired in a step interval of 0.05° (2θ), at the scan rate of 1°/min. The scanning region of the diffraction angle 2θ was 5°–35°, which covers all the significant diffraction peaks of starch crystallites. Samples were used as powders. The relative cristallinity was calculated by dividing the crystalline peak area by the total area[20] following the method described in the literature.[21] The diffractograms were smoothed and the degree of cristallinity ($X_c$) of the samples was quantitatively estimated through integration on Origin 7.0 software.

$$X_c(\%) = \frac{A_c}{A_c + A_A}100 \quad (3)$$

where $A_C$ corresponds to the area of the crystalline peaks and $A_A$ corresponds to the area of the amorphous region.

## Results and Discussion

#### Processing of Maleated Starch

The main consequence of the thermomechanical treatment applied to starch consists in the gelatinization of starch granules. Besides gelatinization, starch macromolecules may suffer degradation.[22] Gelatinization is an irreversible process, which includes granular swelling, melting of granular crystallites, loss of birefringence and amylose solubilization.[23] According to Wang and Chiang, complete gelatinization of starch requires about 70% water content under shearless conditions, whereas gelatinization under shear conditions requires less water because shear stress enhances processing.[24] Some authors have shown that shear stress can result in degradation of starch granules during extrusion.[25] The structural changes may increase the susceptibility of starch to enzyme action, reduce hydrogen bondings and increase the number of free hydroxyl groups. Colonna *et al.* [26] found that the average molecular weight of amylose and amylopectin decreased by factors of 1.5 and 15, respectively, during extrusion.

Figure 1 shows typical changes in torque and temperature as a function of processing time. The tests were conducted at a constant speed of 30 rpm for 8 minutes. The processing temperature was kept at 50 °C. The samples were coded as

 

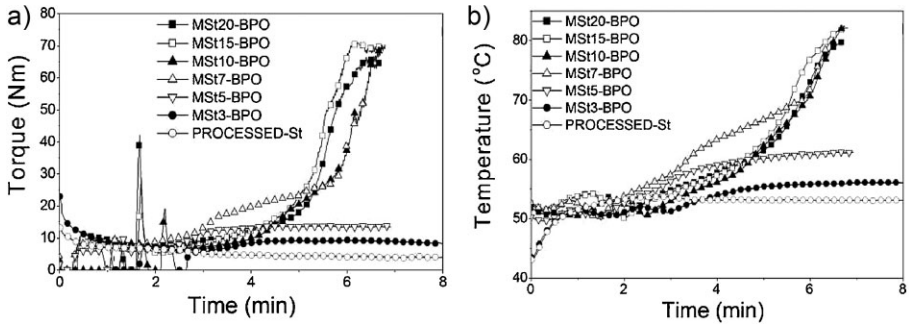


***Figure 1.***
Torque changes (a) and temperature profiles (b) during processing in an internal mixer at 50 °C and 30 rpm for cornstarch without maleic anhydride (○) and for samples with 3% (•), 5% (▽), 7% (Δ), 10% (▲), 15% (□) and 20% (■) MA contents.

MSt(DS)-BPO, where DS represents the theoretical degree of substitution (0, 3, 5, 7, 10, 15 or 20%). Two peaks of torque (Figure 1a) can be seen during processing. In general, the first is associated with loading of the material, and the beginning of processing. The occurrence of a second maximum may be related to partial degradation of starch macromolecules.[27,28] An increase in the MA content produced increments in the loading peak and in the torque values.

The addition of MA at concentrations higher than 20% also increased the heat developed in the reaction, with increasing temperature. The first peak detected is very sharp and results from resistance forces during feeding of cold materials into the mixer. For the samples with 3 and 5% of MA content, this event was followed by stabilization of the torque values, which indicates homogenization of the mixture. It should be noted that, due to shear stress, the temperature increased gradually with reaction time. When the torque values became constant, the temperature profiles for these systems tended to 56.1 and 61.2 °C, respectively (Figure 1b).

The same behavior was not observed for the samples with MA levels above 7%. In such cases, the loading peak was followed by torque decrease and then by a broad peak. This result indicates the initial phase transition of the starch granules under shear stress. The energy produced in the system seems to have provoked loss of crystalline order, with the rupture of granular structure. The applied shear stress and the heat evolved during the exothermic reaction favored granular gelatinization/ melting. Studies by Lai and Kokini (1990)[29] showed that the degree of starch granules rupture is controlled by the plasticizer content, and also by thermal and mechanical energy involved in processing. According to Xue *et. al.*,[30] the second peak represents the maximum point of viscosity caused by granule swelling and gelatinization. After the second peak, most of the starch granules start to pack together, resulting in decreasing torque. The final torque was dependent on water content, mixing speed, and initial temperature. The transient behavior observed in the torque values may be related to the formation and then disruption of agglomerates caused by shear. It was not possible to process samples with MA contents above 20%, under the same reaction conditions using the internal mixer as a chemical reactor. Independently of the MA content incorporated to the mixture, the resulting products were obtained in the powder form.

### Specific Mechanical Energy

SME input depends on material rheology; the higher the viscosity of a material, the higher SME is generally required for processing.[31] This parameter is regularly used to quantify the conversion of mechan-

 

*Table 1.*
SME values for the samples modified with maleic anhydride.

| Sample | MA content (%) | SME (kJ/kg) |
|---|---|---|
| Processed St | – | 168.0 |
| MSt3-BPO | 3 | 242.3 |
| MSt5-BPO | 5 | 304.3 |
| MSt7-BPO | 7 | 500.8 |
| MSt10-BPO | 10 | 452.0 |
| MSt15-BPO | 15 | 604.3 |
| MSt20-BPO | 20 | 518.0 |

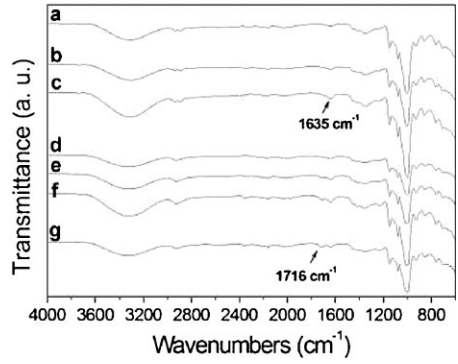


*Figure 2.*
Expanded FTIR spectra of granular corn starch processed without MA (a) and modified with 3% (b), 5% (c), 7% (d), 10% (e), 15% (f) and 20% (g) of MA.

ical energy to thermal energy by a processing equipment. Martin *et al.*[32] observed that higher SME values resulted in lower consistency indeces (K values) of starch and higher power law indeces (n), which means that the starch melts approach Newtonian behavior as the intensity of treatment increased.

The SME values of the samples were determined according to Equation 2, taking into account the total time of processing ($0 < t < 8$ min). The results are presented in Table 1. Under the experimental conditions used, the SME values varied from 168 to 600 kJ/kg, at a constant screw speed. The lowest value of SME was obtained for the sample processed without anhydride, whereas the highest value of SME was obtained for the experiment carried out with 15% MA content at the same temperature. The higher levels of anhydride increased the specific mechanical energy. These results were expected because processing of starch granules without addition of plasticizers is difficult, and requires more energy to be achieved. Therefore, it is reasonable to assume that interaction forces between starch macromolecules are greater when the molecular mobility is low, which contributes to make the material more resistant to flow. The effects of MA content on the specific mechanical energy indicated partial gelatinization of starch granules when processed at higher levels of anhydride. For these experiments, the reaction conditions were chosen within the narrow temperature range between processability and melting of the materials. In this case, the objective was not to obtain a thermoplastic material.

**Infrared Absorption Spectroscopy (FTIR)**

Figure 2 shows the expanded FTIR spectra obtained for the MSt samples, together with that for cornstarch processed in the absence of MA. The unreacted MA was previously extracted from MSt samples through centrifugation carried out in water for 30 minutes at 7500 rpm. For the granular corn starch, a broad and high-intensity band may be observed from 3000 to 3660 $cm^{-1}$, which is attributed to the stretching of starch hydroxyl groups. The absorption at 2927 $cm^{-1}$ corresponds to the deformation of the ring C-H groups. The bands at 930-1160 $cm^{-1}$ are attributed to the C–O stretching in alcohols and C–O-C bending vibrations. The bands located in the fingerprint region between 1018 and 1080 $cm^{-1}$ correspond to O–C bonds in the anhydroglucose units.[33] The band at 1640 $cm^{-1}$ originates from tightly bound water present in starch[11] and the decrease in intensity of this absorption indicates the occurrence of starch chemical modification. The purified MSt samples exhibit a carbonyl stretching peak between 1720–1700 $cm^{-1}$ which corroborates the MA covalent linkage to the starch backbone. The absence of the peak at 1787 $cm^{-1}$, attributed to the ring anhydride carbonyl

 

functions suggests that the MA ring was fully reacted and opened.[12]

Chemical modification reactions of polymers are characterized by low conversions. Conversions of 60% can be considered high. Thus, when the reagent was added in sufficient quantity to react with only 20% of one of the hydroxyl groups of the starch repeating unit of starch (which has three hydroxyl groups), the reaction of 12% of these groups would be expected. As this percentage is equivalent to a very small number of substituted groups, the absorption bands of carboxyl groups introduced in the chain should have low intensity. It should be remarked that the chemical modification reactions were performed in the solid state, directly in the internal mixer, and the degrees of substitution were expected to be very low. The areas under the absorbance peaks at 1710 $cm^{-1}$ (characteristic of the functional group introduced) and 1640 $cm^{-1}$ (characteristic of starch) were determined, and the relative degrees of substitution (RDS) were calculated as the ratio of these areas according to Equation 4. RDS values of 0.11, 0.23, 0.34, 0.36, 0.37 and 0.52 were found, respectively, for the products obtained with 3, 5, 7, 10, 15 and 20% of MA.

$$RDS = \frac{A_{1710}}{A_{1640} + A_{1710}} \quad (4)$$

### X-Ray Diffraction

Starch is essentially made-up of two polymers, amylose and amylopectin. The former is a linear polymer, whereas the latter is highly branched. Starch occurs naturally in the form of granules. These granules vary in size and shape, depending upon the species, and can range in diameter from 1 μm to as large as 120 μm. Most granules are 20–30 μm in diameter.[34] Native starches are biosynthetically assembled as semi-crystalline granules. The type of native, crystalline structure, labeled as A-, B-, or C-type, depends on the starch source. Native A- and B-type crystal lattices consist of double helical, sixfold structures. The difference between the A-type and B-type crystallinity is the packing density of the double helices in the unit cell. Thermoplastic starch that is prepared by extrusion, compression-molding, or injection-molding of several native starches with glycerol as a plasticizer, may exhibit two main types of crystallinity directly after processing: (1) residual crystallinity (native A-, B-, or C-type crystallinity caused by incomplete melting of starch during processing) or (2) processing-induced crystallinity (amylose $V_H$, $V_A$, or V-glycerol-type crystallinity, which is formed during thermo-mechanical processing). The amount of residual crystallinity depends on processing conditions like processing temperature and applied shear stress.[12] Retrogradation, the gradual transformation of starches with a low degree of ordering into a more ordered state, is characterized by a new peak around 17° (2θ).

XRD diffractograms for regular cornstarch and modified starch samples (MSt) samples are shown in Figure 3. Cornstarch shows a typical A-type pattern, with strong reflections at 2θ about 15.7° and 23.8°, and an unresolved doublet at 18.3°, 19.05°. With an increase in anhydride content, the peak at 15.7° (2θ) becomes progressively weaker and broader, whereas the peaks at 18.3° and 19.5° (2θ) merge into a large peak. Similarly, the peak at 23.8° also decreases in intensity. It can be seen that the residual crystalline peaks for the native starch crystals were almost absent, suggesting that the inherent granular, crystalline structure of the native cornstarch was practically disrupted. The loss of crystallinity by the granules, as evidenced by the change in the profile of the diffractograms, is associated with the destruction of the ordered regions.[35] During gelatinization, irreversible physical changes occur in starch granules. The loss of birefringence and crystallinity is characteristic of this process.[36] In the present case, the final products did not show the appearance of a melt, but maintained their powder-like character.

The degree of crystallinity (Table 2) of the samples was determined by the method

 

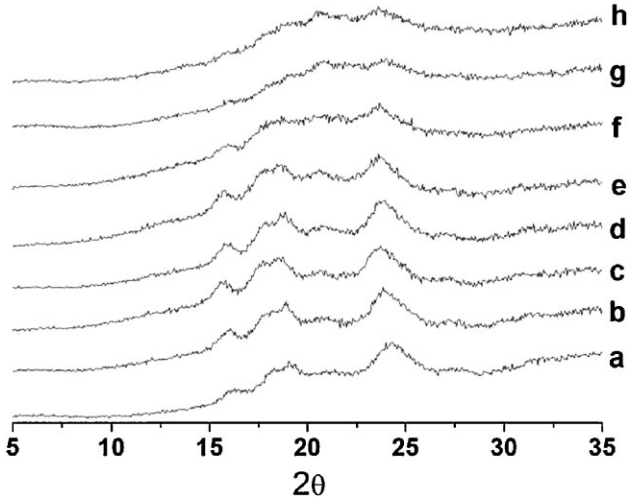


***Figure 3.***
Diffractograms for granular starch (a), for granular starch processed without MA (b) and for MST samples modified with 3% (c), 5% (d), 7% (e), 10% (f), 15% (g) and 20% (h) of MA.

described in the literature.[21] The calculated crystallinities show a strong correlation with the maleic anhydride content incorporated to the samples; the degree of crystallinity being inversely proportional to the anhydride content. The results presented in Table 2 confirm the reduction in crystallinity observed in the XRD patterns of modified products. These results suggest that MA performs an important role in reducing the crystallinity, and does not favor the retrogradation of starch. No new peak around 17° (2θ) appeared in the diffractograms of modified starches, prepared with MA contents higher than 7%.

***Table 2.***
Degree of crystallinity (%) for MSt samples obtained in internal mixer.

| Samples | Degree of crystallinity (%) |
|---|---|
| GranularSt | 21.9 |
| ProcessedSt | 28.1 |
| MSt3-BPO | 24.2 |
| MSt5-BPO | 24.7 |
| MSt7-BPO | 13.3 |
| MSt10-BPO | 10.8 |
| MSt15-BPO | 9.9 |
| MSt20-BPO | 8.8 |

## Conclusion

Novel modified starches were successfully prepared by a simple and environmentally friendly procedure. The modification reaction of starch with MA was carried out at a constant speed and temperature in an internal mixer. FTIR results confirmed the presence of low intensity absorptions at 1710 $cm^{-1}$, characteristic of carboxylic acid groups. The results indicated that the MA content had a significant effect on the characteristics of the processed starch materials. For samples resulting from the reactions of starch with MA contents above 7%, the energy developed in the system appears to have caused the loss of crystalline order, with the consequent disruption of granular structure. For these samples, X-ray diffraction measurements showed almost complete loss of A-type crystallinity. This modification technology proved to be an advantageous technique compared to conventional methods and may extend the possible applications of starch materials.

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