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Note

Microwave processing of natural biopolymers—studies on the properties of different starches

Anikó Szepes [a], Magdolna Hasznos-Nezdei [a], József Kovács [b], Zofia Funke [c], Joachim Ulrich [d], Piroska Szabó-Révész [a,*]

[a] *University of Szeged, Department of Pharmaceutical Technology, Eötvös u. 6, Szeged H-6720, Hungary*
[b] *University of Veszprém, Department of Environmental Engineering and Chemical Technology, P.O.B. 158, Veszprém H-8200, Hungary*
[c] *Martin-Luther-University Halle-Wittenberg, Institute of Bioengineering, D-06099 Halle, Germany*
[d] *Martin-Luther-University Halle-Wittenberg, Institute of Process Engineering, D-06099 Halle, Germany*

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Abstract

In this study, the influence of microwave irradiation on some physico-chemical properties and several pharmaceutical technological parameters of potato and maize starches was investigated. Changes in their habits were observed and decrease in moisture contents caused by the electromagnetic irradiation was determined. The crystalline structures and the micromorphological parameters of the starches were affected by microwave irradiation in different ways depending on the botanical origin of the samples. The tensile strengths of the compacts containing starches were decreased, their wetting properties were enhanced by the thermal process applied. Furthermore, microwave irradiation reduced the surface free energy and the polarity of the compacts significantly. Samples treated by conventional heating were used to compare the effects of microwave irradiation on the examined properties and parameters of these starches.

Keywords: Microwave; Starch; Scanning-electron-microscopy; Surface free energy; X-ray powder diffraction

Applications of microwave energy have been developed primarily for communications and some areas of processing. In pharmaceutical technology, microwave irradiation has been used because of its thermal effect in drying processes (Joshi et al., 1989; Dávid et al., 2000; Pan et al., 2001), for sterilisation of injections and infusions and in a frozen storage-microwave thawing system for intravenous infusions (Sewell and Palmer, 1991a; Sewell et al., 1991b). Several studies focused on the process parameters and the kinetics of microwave drying have been carried out but sufficient data about the effects of electromagnetic irradiation on the structure and physico-chemical properties of frequently used pharmaceutical materials are not available.

* Corresponding author. Tel.: +36 62 545 570; fax: +36 62 545 571.
E-mail address: revesz@pharm.u-szeged.hu (P. Szabó-Révész).

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The objective of the present work was to investigate the morphological parameters and the structural changes of potato (PS) and maize (MS) starches treated by microwave irradiation. The influence of the electromagnetic irradiation on the tensile strengths and surface free energies of compacts pressed from the modified PS and MS was also studied. The initial samples and samples treated by conventional heating were used to compare the effects of microwave irradiation on the examined properties and parameters of these starches.

PS and MS were used as experimental materials (Hungaropharma, Budapest, Hungary). Physical modifications were achieved in two different ways:

- by microwave irradiation for 15 min in a Sharp R4P58 (450 W) microwave oven (PS_{mw} and MS_{mw});
- by conventional heating at 130 °C for 2 h ($PS_{130\,°C}$ and $MS_{130\,°C}$) in a drying oven without air flow (Fortuna et al., 1998; Palasinski et al., 2000).

In both cases, 100.0 g powder was modified. The initial and the treated samples were stored in well-closed vessels at room temperature (20 ± 2 °C; 45 ± 5% RH).

The moisture contents of the samples were determined by using the HR73 Halogen Moisture Analyzer (Mettler-Toledo GmbH, Greifensee, Switzerland) at 60 °C.

The particle form and particle surface of the starches were investigated by SEM (Philips XL 30 ESEM).

The micromorphological parameters of the samples were determined using Micromeritics ASA 2000 equipment (Instrument Corp., Norcross, GA, USA) from the data of nitrogen adsorption and desorption isotherms at the boiling point of liquid nitrogen under atmospheric pressure (−196 °C). The specific surface areas (F_{BET}) and mesopore diameters (D (4V/F)) were calculated in the validity range of the BET-isotherm. The mesopore volumes ($V_{P\,1.7–300\,nm}$) were calculated via the BJH-method.

The particle size and its distribution for all samples were measured by laser diffraction (Malvern Mastersizer 2000, Malvern Ltd., Worcestershire, UK).

The powder X-ray diffraction profiles were taken using an X-ray diffractometer (Philips PW 1050/70 PW 1710) under the following conditions: radiation source: Cu Kα, scan speed: $0.035\,2\theta\,s^{-1}$, step size: $0.035\,2\theta\,s^{-1}$, time per step: 1.0 s.

Binary powder mixtures were prepared by mixing 80% (w/w) microcrystalline cellulose (Avicel® PH 101, FMC Corp., Philadelphia, USA) and 20% (w/w) starch in a Turbula mixer (Willy A. Bachofen, Maschinenfabrik, Basel, Switzerland) at 50 rpm during 2 min. Compacts were compressed with an instrumented eccentric tabletting machine (Korsch EK0, Berlin, Germany).

The crushing strengths of the tablets were measured using Heberlein equipment (Heberlein and Co. AG, Zürich, Switzerland), while tensile strengths were calculated via the equation of Fell and Newton (Fell and Newton, 1970).

The surface free energies of the tablets were determined by contact angle measurements with polar (bidistilled water) and non-polar (diiodomethane, Merck KGaA, Darmstadt, Germany) liquids, using the OCA 20 Optical Contact Angle Measuring System (Dataphysics, Filderstadt, Germany) with the sessile drop method. Surface free energies were calculated via the Owens–Wendt equation (Owens and Wendt, 1969).

Porosity parameters of the tablets were determined by a high-pressure mercury porosimeter (PASCAL 140 + 440, Porotec GmbH, Hofheim, Germany).

The difference between sample means was deemed statistically significant if the 95% confidence intervals for the means did not overlap.

The particles of the initial PS (23–75 μm) were ovoid and had a smooth surface (Fig. 1a). The microscopic pictures of the microwaved PS did not reveal noteworthy changes (Fig. 1b). Heating of potato starch at 130 °C caused cracks in the surface of the particles (Fig. 1c).

The particles of the MS were smaller (9–23 μm) and had a crystalline appearance (Fig. 2a). The unmodified MS sample consisted of non-agglomerated crystalline particles. The particles were deformed after microwave irradiation (Fig. 2b) and conventional heating, and formed loose agglomerates (Fig. 2c). These observations are in good agreement with the results obtained by Palasinski et al. (2000).

The physical treatments applied did not cause remarkable changes in particle size and particle size distribution of the starches (Table 1).

The micromorphological parameters of the PS and MS were entirely different (Table 1), which can be related to the structural differences of the samples (Swarbrick and Boylan, 2002). The micromeritics of PS were changed slightly during the thermal processes. The specific surface area of the MS modified

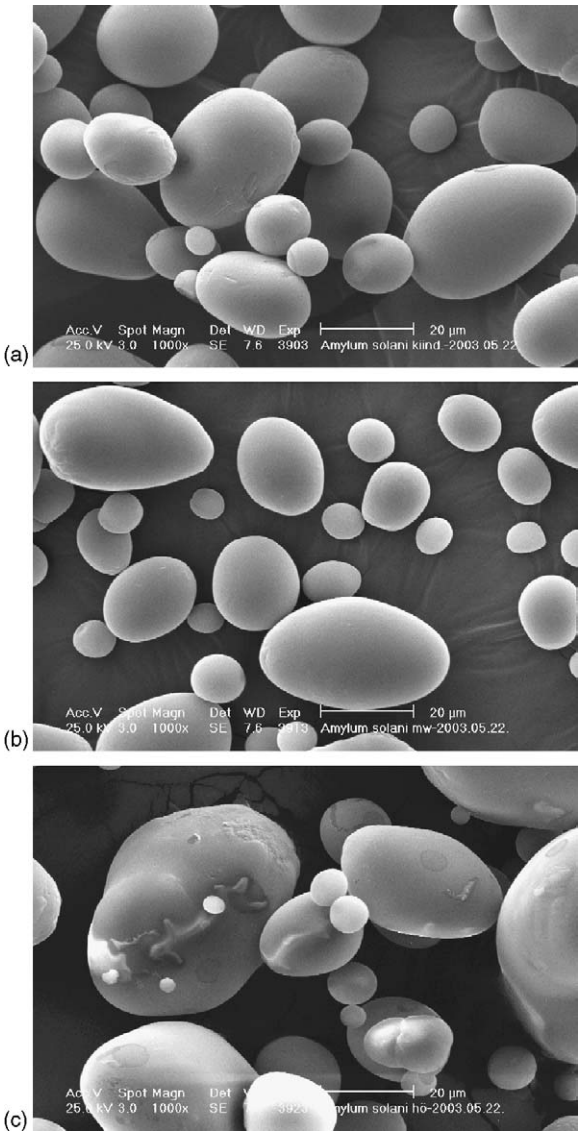

Fig. 1. SEM pictures of potato starch. (a) PS; (b) PS_{mw}; (c) PS_{130°.

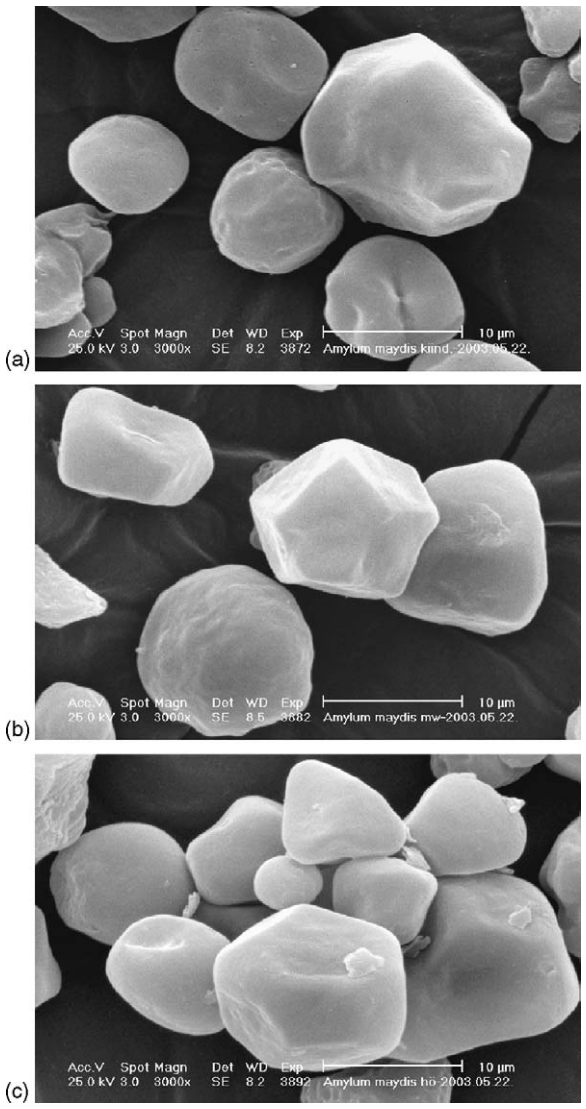

Fig. 2. SEM pictures of maize starch. (a) MS; (b) MS_{mw}; (c) MS_{130°.

Table 1
Parameters of starch samples ($n = 3$)

Samples	Moisture content (%)	$D_{10\%}$ (μm)	$D_{90\%}$ (μm)	F_{BET} (m^2/g)	$V_{P\ 1.7–300\ nm}$ ($\times 10^{-4}\ m^3/g$)	D (4V/F) (nm)
PS	9.66 ± 0.20	23.47 ± 0.08	75.62 ± 0.07	0.12 ± 0.002	1.83	11.5
PS_{mw}	0.07 ± 0.00	23.16 ± 0.02	73.86 ± 0.07	0.10 ± 0.003	1.66	7.55
$PS_{130\ ^\circ C}$	0.60 ± 0.11	23.82 ± 0.30	73.16 ± 0.04	0.11 ± 0.002	1.73	8.47
MS	6.84 ± 0.14	9.39 ± 0.22	23.02 ± 0.31	0.27 ± 0.004	9.11	13.50
MS_{mw}	0.00 ± 0.00	9.33 ± 0.01	22.51 ± 0.07	0.30 ± 0.003	9.17	13.00
$MS_{130\ ^\circ C}$	0.01 ± 0.01	9.34 ± 0.02	22.41 ± 0.14	0.38 ± 0.003	11.60	9.42

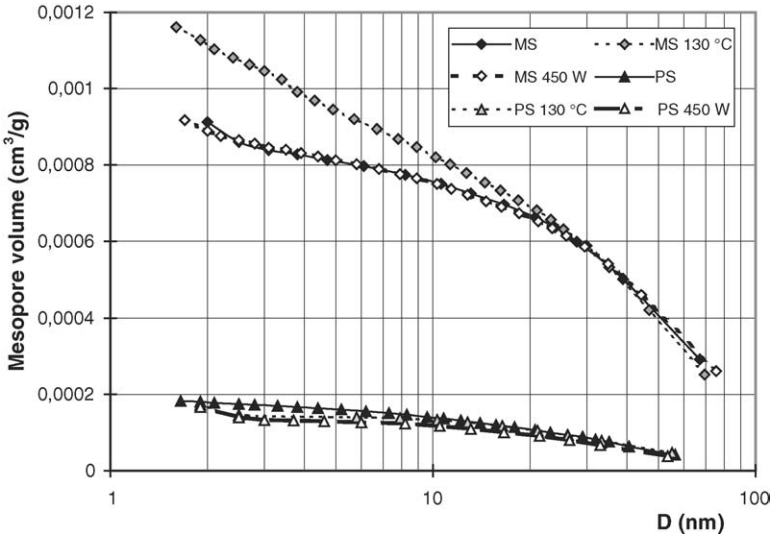

Fig. 3. Cumulative mesopore volume distributions of starch samples as a function of average mesopore diameter (*D*).

by conventional heating ($MS_{130\,^{\circ}C}$) became 40% larger and a similar significant increase was observed on evaluation of the mesopore volume data (30%). The changes in micromorphology of MS were considerable smaller after microwave irradiation (MS_{mw}). Differences between the microstructures of the starch samples are well demonstrated by the cumulative mesopore volume distribution curves (Fig. 3).

The crystallinity of PS increased during microwave irradiation, while conventional heating tended to destroy the crystalline structure (Table 2). The unmodified MS contained a higher crystalline fraction (84.6%). This fell to 30% during microwave irradiation and to 33% during conventional heating (Table 2). These results are in agreement with previous investigations which proved that the crystal structure of the PS changed from the B pattern to the A pattern. Typically, tuber starches exhibit the B type of crystallinity, whereas cereal starches display the A type of crystal structure (Lewandowicz et al., 1997, 2000; Swarbrick and Boylan, 2002).

Table 2
Results of X-ray examinations of starch samples

Samples	2Θ (°)	Intensity/ crystalline part (cps)	Intensity/ amorphous part (cps)
PS	17.185	5776	4665
PS_{mw}	17.135	6147	3114
$PS_{130\,^{\circ}C}$	16.905	3906	5227
MS	22.850	6115	1116
MS_{mw}	22.755	2116	4956
$MS_{130\,^{\circ}C}$	22.860	2490	4970

2Θ: reflection angle.

As compared with the compacts consisting of microcrystalline cellulose only (AV), the application of the initial starches for tablet formulation decreased the tensile strengths of the compacts, and the tensile strengths were also decreased after physical treatments (Table 3). The extent of the decrease did not depend on the type of starch applied, but the effects of the thermal modifications on the tensile parameters differed. The decrease in the tensile strength caused by the application of thermally modified PS was more significant than the decreases in the strength parameters of the comprimates containing physically treated MS. The experimental results of MS could be related to its special structure. MS is more resistant towards modifying agents than is PS, which is probably due to the occurrence of lipids in the surface and helical amylose complexes (Fortuna et al., 1998).

The solids containing the initial PS had smaller contact angles than those compressed from the unmodified MS (Table 4). The lower hydrophilicity of MS could be attributed to the lipid content and the special structure of this starch type (van Oss, 1995). The effects of the microwaved PS and MS on the contact angles were

Table 3
Influence of starches on physical parameters of compacts containing 20% starch and 80% microcrystalline cellulose (Avicel® PH 101) (compression force = 2 ± 0.5 kN) (n = 10)

Compacts	Average mass (g)	Average height (mm)	Average tensile strength (MPa)
Avicel® PH 101 (AV)	0.2157 ± 0.0050	2.33 ± 0.02	5.46 ± 0.09
AV/PS	0.2149 ± 0.0012	2.51 ± 0.02	4.60 ± 0.24
AV/PS_{mw}	0.2237 ± 0.0012	2.64 ± 0.01	4.00 ± 0.22
AV/$PS_{130\,°C}$	0.2172 ± 0.0011	2.79 ± 0.01	3.46 ± 0.13
AV/MS	0.2099 ± 0.0031	2.34 ± 0.04	4.83 ± 0.44
AV/MS_{mw}	0.2158 ± 0.0073	2.40 ± 0.05	4.31 ± 0.35
AV/$MS_{130\,°C}$	0.2224 ± 0.0011	2.48 ± 0.02	4.43 ± 0.14

Table 4
Contact angles and surface free energies of compacts with a porosity of 10 ± 2% containing 20% starch and 80% microcrystalline cellulose (Avicel® PH 101) (compression force = 20 ± 1 kN) (n = 10)

Compacts	Θ_{water} (°)	$\Theta_{diiodomethane}$ (°)	γ^d (mN/m)	γ^p (mN/m)	γ (mN/m)	Polarity[a] (%)
Avicel® PH 101 (AV)	38.83 ± 1.77	25.02 ± 0.66	33.69	27.81	61.49	45.23
AV/PS	33.00 ± 1.40	24.46 ± 0.70	32.72	31.72	64.44	49.22
AV/PS_{mw}	47.20 ± 1.97	33.08 ± 0.77	31.81	23.28	55.09	42.26
AV/$PS_{130\,°C}$	44.84 ± 1.02	37.59 ± 1.65	31.87	25.21	57.08	44.17
AV/MS	34.47 ± 1.78	25.24 ± 1.12	33.21	30.60	63.80	47.96
AV/MS_{mw}	45.03 ± 1.48	33.13 ± 1.20	31.44	25.33	56.77	44.62
AV/$MS_{130\,°C}$	53.51 ± 1.76	32.05 ± 1.53	30.90	20.19	51.09	39.52

γ: surface free energy; γ^d: surface free energy disperse part; γ^p: surface free energy polar part; Θ: contact angle.
[a] Polarity = $(\gamma^p/\gamma) \times 100$ (Oh and Luner, 1999).

significant and had the same scale, while application of the MS treated by conductive heating resulted in larger changes in the contact angles than those for the PS. The decreased hydrophilicity of the processed starches could be explained by the fact that thermal treatment decreases the content of the more hydrophilic structure polymer ("amylose-escape") (Lewandowicz et al., 1997, 2000; Palasinski et al., 2000).

Both the microwave irradiation and the conventional heating reduced the surface free energy and the polarity of the compacts, which was due to the water loss from the starches caused by the thermal treatment (Table 1). The disperse and polar parts of the surface free energies of the initial samples were nearly equal. After the thermal processes, the polar components fell drastically, whereas the disperse part did not decrease significantly (Table 4).

According to previous studies, the susceptibility of starches to the hydrothermal processes depended on their botanical origin. Our results allow the conclusion that the difference in response of PS and MS to the microwave irradiation was related to the structural difference of the initial starches. Furthermore, the samples responded differently to the two hydrothermal treatments, again the crystallinity might be a decisive factor. The changes in tensile strength, wettability and surface free energy could be attributed to the water loss (dehydration) during microwave treatment. On the other hand, irreversible structural changes caused by the physical treatments, such as crystalline–amorphous solid phase transition and "amylose-escape" may have an influence on the above properties.

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