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Structural modifications of low hydrated pea starch subjected to high thermomechanical processing

C. Barron, A. Buleon, P. Colonna, G. Della Valle*

Unite de Recherches sur les Polysaccharides Leurs Org. et Inte., Inst. Nat. de Recherche Agronomique, 71627-44316 Nantes, Cedex 03, France

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Abstract

A pre-shearing rheometer, the Rheoplast®, was used to perform thermomechanical processing and simulate extrusion-cooking. Under various well-controlled conditions of thermal and mechanical (60–370 J g^{-1}) inputs, native pea starch (moisture content MC = 25 and 30%) was processed at temperatures below and above the melting endotherm determined by differential scanning calorimetry (DSC). The extent of starch transformation was studied at macroscopic, granular, crystalline and macromolecular levels by light microscopy, X-ray diffractometry, DSC and intrinsic viscosity, respectively. Incomplete transformations were obtained for lower temperatures. Crystalline structure was greatly modified, showing partial melting with a higher sensitivity of the B-type crystalline structure. Melting of starch granules began near the hilum without swelling. No mechanical effects of shearing were observed on granular or crystalline structures, although conversion of mechanical energy into heat apparently occurred either by solid friction or viscous dissipation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Starch; Extrusion; Melting; Shear; Crystallite; Granule

1. Introduction

During extrusion, a divided solid is plasticized or melted and then shaped to create, for instance, a solid foam texture. When this process is applied to starch, all structural features are modified (Colonna & Buleon, 1994). The granular structure is lost, native crystals are melted, and macromolecules are partially disrupted. Depending on the processing conditions, new structures can appear, such as amylose/lipid complexes, at the crystalline or amorphous state, or unstable E-type crystalline structures (Mercier, Charbonnière, Gallant & Guilbot, 1979; Singh, Cairns, Morris & Smith, 1998). Many studies have related the final state of starch transformation to such processing parameters as screw geometry, barrel temperature or water content of the product (Colonna, Tayeb & Mercier, 1989). However, material is modified all along the screw, as shown by a concomitant decrease in intrinsic viscosity and an increase in the degree of gelatinization in samples taken after dead-stop experiments (Cai & Diosady, 1993; Colonna, Melcion, Vergnes & Mercier, 1983; Davidson, Paton, Diosady & Larocque, 1984). In single-screw extrusion, this transformation is progressive. For polymers, a molten film develops close to the barrel, thickens and then forms a liquid pocket that accumulates polymers at the back of the channel (Tadmor, 1966). The mechanisms for obtaining the molten phase in these conditions have been largely studied and modeled for synthetic polymers. Conversely, twin-screw extrusion is characterized by a very short melting zone. The transformations that occur in this transition section are difficult to analyze experimentally with respect to instrumentation and sampling. Melting is initiated as soon as the first restrictive screw element (die, reverse screw element, kneading blocks) is encountered after feeding (Barres, Vergnes, Tayeb & Della Valle, 1990; Colonna et al., 1983). Powder is compacted, and a powder + melt mix and then a homogeneous molten phase are obtained in a very short time (3–10 s) under a high shearing rate ($\approx 100\ s^{-1}$). The molten phase is conveyed afterwards. This most active zone of the extruder, which is usually 2 or 3 C-chambers long, has been very briefly described in theoretical models of twin-screw extrusion (Della Valle, Barres, Plewa, Tayeb & Vergnes, 1993). A better understanding of the mechanisms involved in the modification of starch in such conditions should improve the performance of these models and facilitate the choice of raw materials for extrusion.

One of the notable peculiarities of the extrusion process is that thermal transitions take place at low moisture contents

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* Corresponding author.

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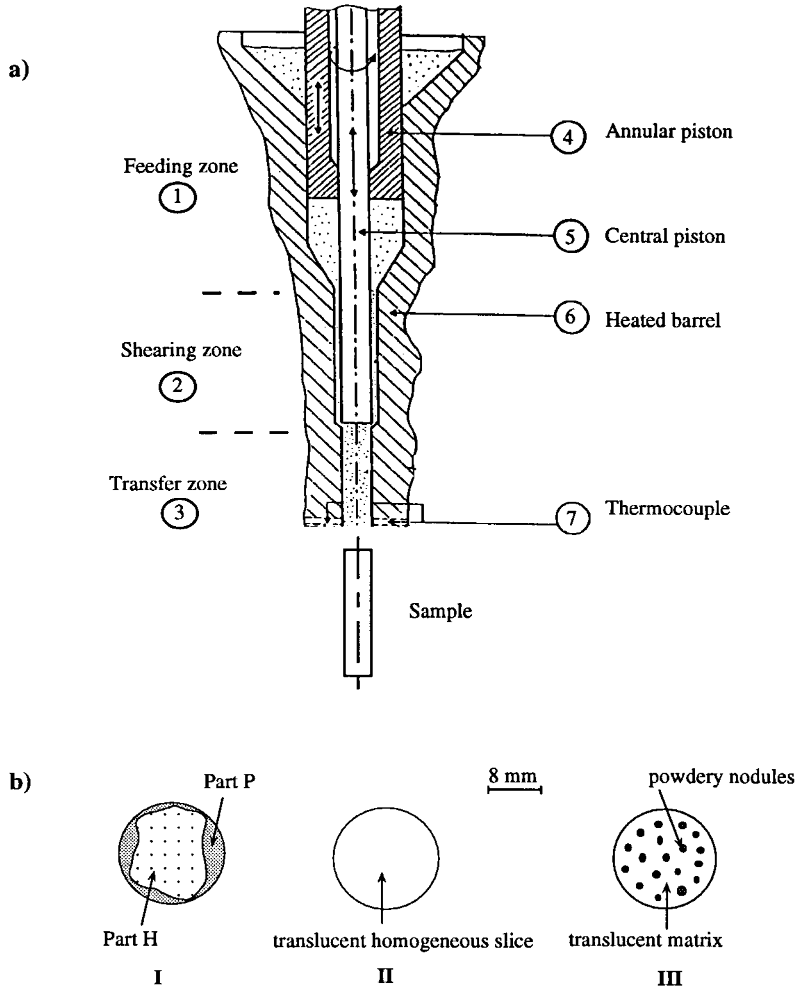

Fig. 1. (a) Diagram of the Rheoplast®. Dotted zone indicates material being processed. (b) Enlarged axial sections of rod sample according to processing conditions: I. mechanical process at $T < T_p$; II. mechanical process at $T > T_p$; III. no mechanical process—$T > T_p$.

(10–35% wb). Phase transitions have been largely studied by differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS) and microscopy, although the experimental conditions involved were not very similar to those encountered in extrusion with respect to combined heating kinetics and shearing rate. Various transitions were observed depending on water content (Donovan, 1979), which were attributed to different types of melting behavior, recrystallizations or polymorphic transitions (Biliaderis, 1992).

Few studies have focused on the structural modifications of starchy products during thermomechanical processing. Such studies require an experimental tool to create the intermediate steps in transformation and analysis of the modifications on different structural scales. Yam, Gogoi, Karwe and Wang (1994) used instrumented twin-screw extruders to show the effect of shearing on the transformation of the starchy fraction of corn meal, as evaluated by DSC. Zheng, Chaing and Wang (1995) used single-screw extrusion performed at low temperature to demonstrate the importance of this phenomenon on granular size and the degree of cooking as defined by the relative decrease of melting enthalpy determined by DSC. Zheng and Wang (1994) also simulated thermomechanical processing using a capillary rheometer. Thermal energy was applied before mechanical processing, and the high shearing rates obtained led to low residence times in the capillary. All these works were only based on DSC measurements which provide an incomplete description of starch modifications. Fujio, Igura and Hayakawa (1995) used a similar experimental device to show the impact of shearing on the macromolecular degradation of starches of various botanical origins. Vergnes, Villemaire, Colonna and Tayeb (1987) simulated the real transformation process using a pre-shearing rheometer. The products obtained had structural features similar to those achieved after extrusion, as determined by WAXS and intrinsic viscosity. The analogy with extrusion-cooking was confirmed by studies of changes in properties in excess of water. However, modifications occurring at all structural levels have rarely been taken into account, and the hypothetical mechanism of transformation proposed by Gomez and Aguilera (1984) has never been precisely described.

These authors considered extruded starch as a blend of gelatinized and dextrinized starches resulting from gelatinization of granules (with associated swelling, despite the low water content) and/or fragmentation of granules, but they observed no intermediate transformation stages. It is still uncertain which structural level is first modified by this type of processing.

The purpose of the present study was to define the mechanisms for obtaining a starchy molten phase under thermomechanical processing similar to extrusion-cooking, i.e. melting or mechanical particle disintegration (by surface erosion or shattering; Peleg, 1992). A pre-shearing rheometer (Rheoplast®) was used to simulate extrusion and achieve intermediate transformation stages characterized on four structural scales (macroscopic, granular, crystalline and molecular). Smooth pea starch was used as the model substrate because of its low lipid content and very promising performance as a raw material for non-food applications (Lourdin, Della Valle & Colonna, 1995).

2. Materials and methods

2.1. Materials

Smooth pea starch was a commercial product (Nastar from Cosucra, Belgium) with an initial moisture content (MC) of 10.7% (wb) conditioned to MC = 25 and 30% (wb) by progressive addition of water under stirring. Amylose content was 37% as determined by the amylose–lysolecithin complex method (Mestres, Matencio, Pons, Yajid & Fliedel, 1996). Lipid content was low (<0.1%), and granules were large (median diameter: 30.4 μm).

2.2. Thermomechanical processing

Thermomechanical processing was performed using a pre-shearing rheometer, the Rheoplast®, a proven means of simulating extrusion-cooking (Vergnes et al., 1987). Starch was transformed both by mechanical shearing (in a Couette rotational system) and by heat conduction from the barrel.

This experimental device contained three separate zones (Fig. 1a). Starch descends from the feeding (1) to the shearing zone (∅ = 21 mm) (2) by gravity and under the force of an annular piston (4). The shearing zone is closed off at the bottom by the inner piston (∅ = 16 mm) (5) and then filled, producing a 2.5 mm thick layer. After compaction (by the annular piston), starch is transformed for a defined period (Δt) by rotation of the inner piston (at a pre-determined velocity Ω). The inner piston then rises, opening up a clearance area at the bottom of the cylindrical zone. The processed material is forced down into the transfer zone by the annular piston (3) and then evacuated by the inner piston at a constant velocity (4 mm s^{-1}). Both pistons return to their initial positions and the whole operating sequences define a cycle. Melting viscosity was not measured after processing, and no capillary system was added. Samples were recovered in the same state as immediately after shearing in the Couette zone.

Volumes in the shearing and transfer zones were identical (10 cm^3). About 15 g of powdery starch were processed in one batch. Barrel temperature (6) was adjusted using a heating element, and sample temperature was measured with a thermocouple at the end of the transfer zone (7). The temperature was further measured by a needle thermocouple immersed in the sample just after recovery. Torque resulting from opposition of the material to the rotation of the inner piston was recorded throughout the experiment, allowing specific mechanical energy (SME) to be determined: $\mathrm{SME} = ((C_a \times \Delta t \times \Omega)/m)$ where C_a is the average torque (N m), Δt the shearing duration (s), Ω rotation velocity (rad s^{-1}) and m the weight of treated material (g).

Recovered samples were shaped like cylindrical thick rods ($L \approx 5$ cm; $\varnothing \approx 16$ mm), whose approximate density, as evaluated by weighing and size measurements using a vernier calliper, was between 1200 and 1300 kg m^{-3}. The samples were cut into thin slices and dried at 40°C under vacuum for 24 h. They were later immersed for 3 h in a definite quantity of deionized water. Sometimes part of the sample could be removed from the bulk and recovered in suspension, whereas the other part remained cohesive. If both fractions were obtained, they were separated by wet-sieving. The suspension was centrifuged at 600*g* for 10 min and then dried by solvent exchange. The cohesive part was dried and ground in a liquid nitrogen-cooled grinder. Finally, samples were sieved (500 μm) before further analysis.

2.3. Analytical methods

Macromolecular degradation was evaluated by intrinsic viscosity values. Measurements were performed at 25°C in 0.2 N KOH with an automatic Ubbelhode viscosimeter (solvent elution time: 174 s). Concentration ranges were 0.6–3.6 mg ml^{-1}, and the initial starch concentration was measured by the orcinol–sulfuric acid method (Planchot, Colonna & Saulnier, 1997a).

Differential scanning calorimetry was used to determine gelatinization enthalpy in excess of water and the melting transition temperatures under varying water contents. DSC experiments were performed with a DSC 121 instrument (Setaram, France). For gelatinization enthalpy measurements, 20 mg of sample together with 100 mg of deionized water was heated from 5 to 165°C at a rate of 3°C min^{-1}. Melting was determined at various moisture contents between 5 and 180°C at the same heating rate. Samples with required moisture content were prepared directly in stainless-steel pans by addition of a defined quantity of water to native starch. The pans were centrifuged at 600*g* for 10 min and then allowed to equilibrate overnight at 4°C before measurement.

X-Ray diffractometry measurements were performed with Inel (France) X-ray equipment at 40 kV and 30 mA.

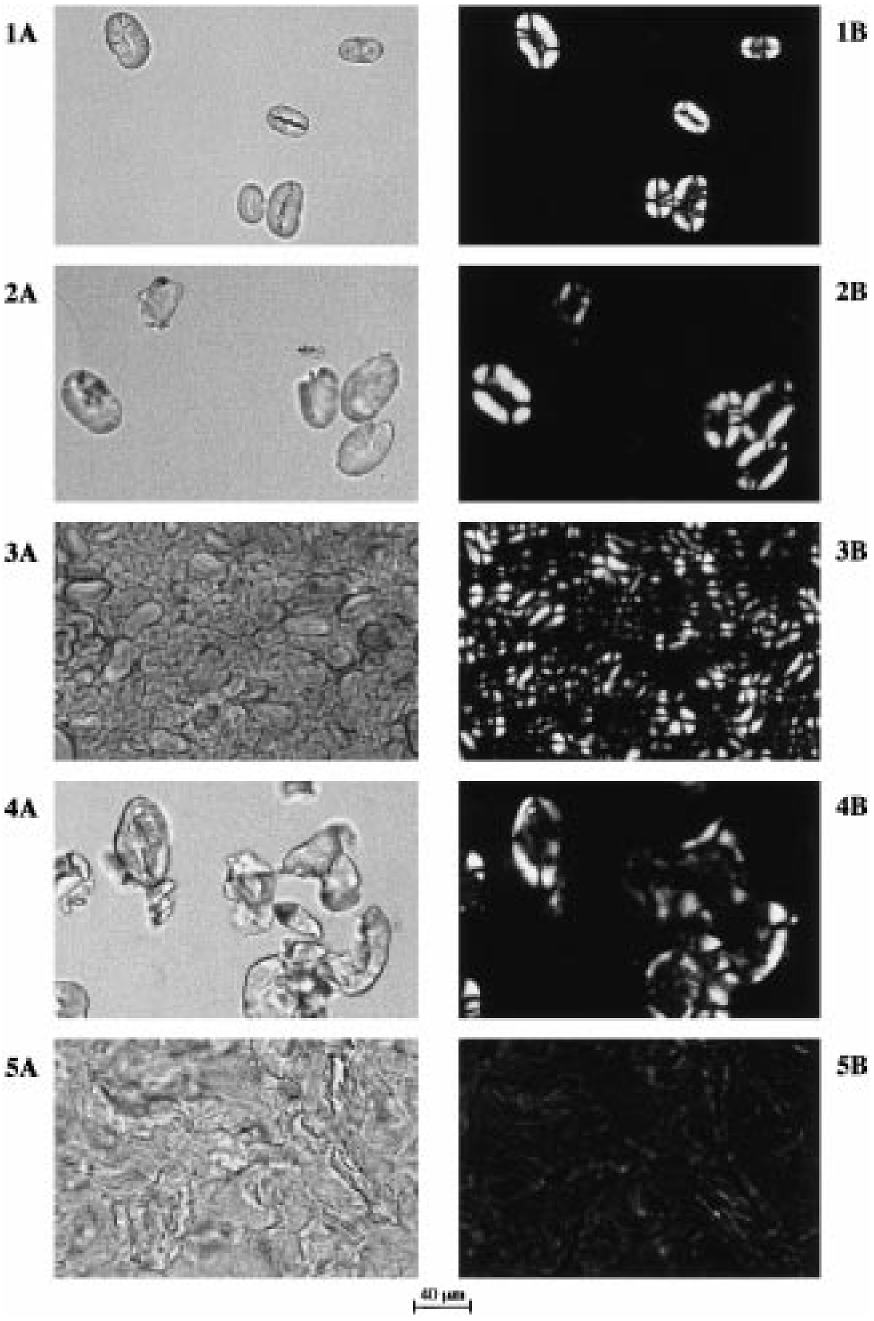

Fig. 2. Microscopic observations of smooth pea starch transformed in the Rheoplast® in (a) natural or (b) polarized light. (1) native; (2) $T = 95°C$, part P, (3) $T = 95°C$, part H, (4) $T = 25°C$, (5) $T = 150°C$ and mechanical processing.

$CuK\alpha_1$ radiation ($\lambda = 0.15045$ nm) was selected using a quartz monochromator. A curved position-sensitive detector (Inel CPS 120) was used to monitor diffracted intensities over a 2 h exposure period. After hydration on saturated $BaCl_2$ solution at 25°C ($a_w = 0.9$) for one week, samples (40 mg) were sealed between sticking tapes to prevent any significant water loss during measurement. Water content was determined on aliquots after drying for 2 h at 130°C. After equilibration, all moisture contents were similar (20–21% wb). The crystallinity ratio and the amount of A- and B-type structures were determined by applying a multilinear regression procedure based on that used by Gernat, Radosta, Damaschun and Schierbaum (1990), with $a \pm 5\%$ error. This method assumes that experimental normalized diagrams are a linear combination of three elementary patterns: amorphous, A- and B-types. A- and B-type spherulites were taken as crystalline references, and extruded pea starch as the amorphous reference. Diffraction diagrams were all normalized at the same total scattering value, with 2θ ranging from 3 to 30°.

Light microscopy was performed with a Leica microscope. Slices were first hydrated to allow semi-thin sections

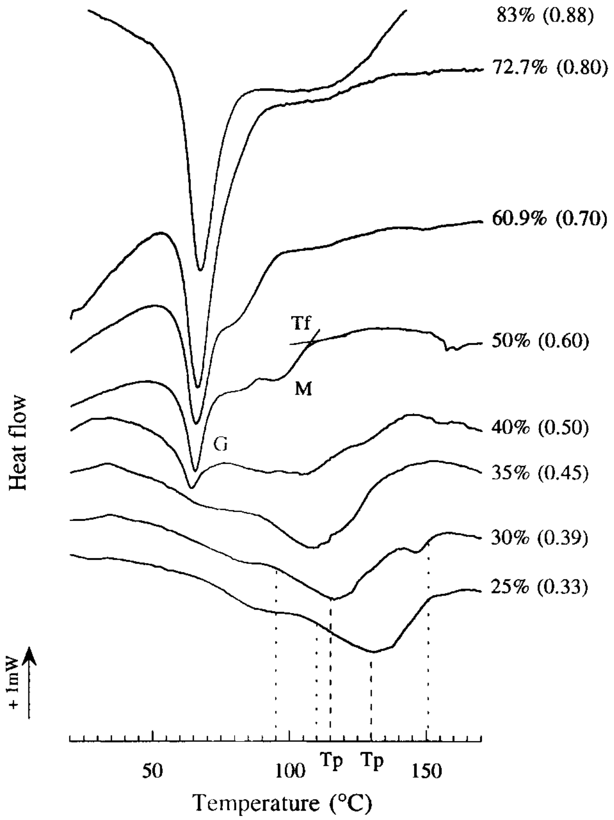

Fig. 3. DSC-thermograms of smooth pea starch at various moisture contents (wb). The volumic fraction of water is given in parentheses. Definition of T_p: peak temperature and processing temperatures: $T < T_p$ (95–110°C) and $T > T_p$ (150°C) at MC equal to 30 and 25% (wb).

(10 μm thick) to be cut with a cryotome (Microm HM 500 OM) after quenching at −55°C. Sections were then dried at 40°C and stained with Congo red (1%) to reveal damaged granules. Sections were examined under natural or polarized light to show the radial orientation of starch granules.

Changes on a macroscopic scale were determined by visual examination of slices recovered from an extruded rod. The kinetics of iodine sorption was evaluated after exposure of samples to a highly hydrated atmosphere. Iodine sublimation occurred for each sample during the same time period (10–15 min). Variations in staining were then observed.

3. Results and discussion

3.1. Assessment of the processing and sampling method

With the Rheoplast®, 15 g of starch was batch-processed under well-controlled conditions. The temperature measured in the thick rod was always about 10°C lower than the barrel temperature. For the same processing conditions, torque resulting from the opposition of material to the rotation of the central piston was similar (a coefficient of variation between 3 and 12% depending on kinematic conditions). No significant variation in intrinsic viscosity was observed for different samples obtained under the same processing conditions, and variations in residual gelatinization enthalpy were much lower than those determined on samples obtained when processing conditions differed. Thus a good repeatability between successive cycles was achieved.

Rod structure was stabilized by drying at low temperature. After equilibration under normal atmospheric conditions, samples had a water content of between 8 and 12% (wb). Zeleznak and Hoseney (1987) found, in these moisture contents, that values for glass transition temperature ($T_g \approx$ 70–120°C) were clearly higher than the storage temperature (25°C), regardless of the structural state of starch, whether native or gelatinized. No trace of retrogradation was shown by WAXS or DSC. While microscopy or WAXS analysis can be performed on slices, methods such as DSC need to be done with powdery samples. As rods were very compact (specific gravity around 1.25) and difficult to grind with a mortar (pounding), freeze-grinding had to be used. This procedure produced no significant decrease in intrinsic viscosity value or residual gelatinization enthalpy as compared to a milder but more tedious method (lyophilization and pounding).

Consequently, the experimental device allowed a low quantity of starch (15 g) to be batch-processed under well-defined conditions. The sampling protocol provided good stabilization of all structural features, which could have been related to the treatment performed.

3.2. Structural characteristics of native starch

Starch granules observed in light microscopy were simple, large, and either oval or sphere-shaped. Internal fissures were observed in many granules (Fig. 2; (1)), which could have been due to the industrial extraction process, as reported by Stute (1990). Under polarized light, all granules were strongly birefringent. A typical C-type crystalline structure was observed by X-ray diffractometry. The total crystallinity ratio was 36% (±5%), a value much higher than that obtained by Gernat et al. (1990) or by Cairns, Bogrecheva, Ring, Hedley and Morris (1997), respectively 19 and 21% (±2%). However, the moisture content of their samples during X-ray diffractometry experiments was lower and that could induce an underestimate of crystallinity ratio (Cleven, van der Berg & van der Plas, 1978). The polymorphic composition in our study was similar to that obtained by these authors, i.e. the A- and B-types represented, respectively 65 and 35%, corresponding in our case to 24% of A-type and 12% of B-type structure on a total starch basis. The intrinsic viscosity value of native starch was 228 ± 10 ml g^{-1}.

Thermal transitions of pea starch were determined for various moisture contents in order to provide critical reference temperatures for thermomechanical processing (Fig. 3). Above 70% of water, only one endothermic event

Table 1
Structural features of smooth pea starch transformed in the Rheoplast® (MC, moisture content; T, barrel temperature; Ω, rotation velocity of the inner piston; Δt, duration of treatments; CR, Congo red staining (positive or not); Biref., birefringence (existing or not); Crystal. ratio, crystallinity ratio (%); ΔH, enthalpy of gelatinization in excess of water (absolute value); T_{max}, peak temperature; ΔT, width of endothermic peak; nd, not determined)

Exp. #	MC	T (°C)	Ω (rpm)	Δt (s)	SME (J g^{-1})	Macroscopic	Microscopic		X-ray diffractometry			DSC in excess of water			Intrinsic viscosity (ml g^{-1})
							CR	Biref.	Crystal. ratio	%B	%A	ΔH (J g^{-1})	T_{max}(°C)	ΔT (°C)	
Native						Powder	−	+	36	12	24	13.6	66.8	19.6	228
1	0.25	110	50	15	61	Powder	+/−	+	nd	nd	nd	5.8	75.5	15.7	219
						Melt	+	+	28	3	25	3.0	73.4	15.8	225
2	0.25	110	50	30	270	Powder	+/−	+	nd	nd	nd	6.9	71.0	15.4	239
						Melt	+	+	nd	nd	nd	5.0	71.9	13.5	221
3	0.25	110	100	30	234	Powder	+/−	+	nd	nd	nd	6.2	72.0	15.9	214
						Melt	+	+	nd	nd	nd	5.9	72.3	15.4	217
4	0.25	150	100	30	154	Melt	+	−	0			0			200
5	0.30	25	200	30	1000	Powder	+	+	18	3	15	2.8	68.3	26.8	193
6	0.30	95	50	15	80	Powder	+/−	+	nd	nd	nd	6.6	73.8	13.7	219
						Melt	+	+	23	3	20	6.1	75.0	14.6	220
7	0.30	95	50	30	90	Powder	+/−	+	28	4	24	7.0	73.1	15.1	201
						Melt	+	+	27	4	22	5.6	75.6	14.2	195
8	0.30	95	100	15	173	Powder	+/−	+	25	5	20	6.9	72.1	12.7	187
						Melt	+	+	25	4	21	4.5	74.5	13.5	209
9	0.30	95	100	30	177	Powder	+/−	+	27	4	23	6.9	73.3	11.3	196
						Melt	+	+	23	5	18	3.2	76.0	14.6	204
10	0.30	95	200	30	372	Powder	+/−	+	nd	nd	nd	6.4	71.8	13.1	nd
						Melt	+	+	26	8	18	5.0	73.8	14.6	202
11	0.30	150	50	15	75	Melt	+	−	0			0			205
12	0.30	150	50	30	75	Melt	+	−	0			0			195
13	0.30	150	100	30	178	Melt	+	−	0			0			203
14	0.30	150	0	60	0	Heterogeneous	+	+	14	4	10	2.5	76.6	16.8	229

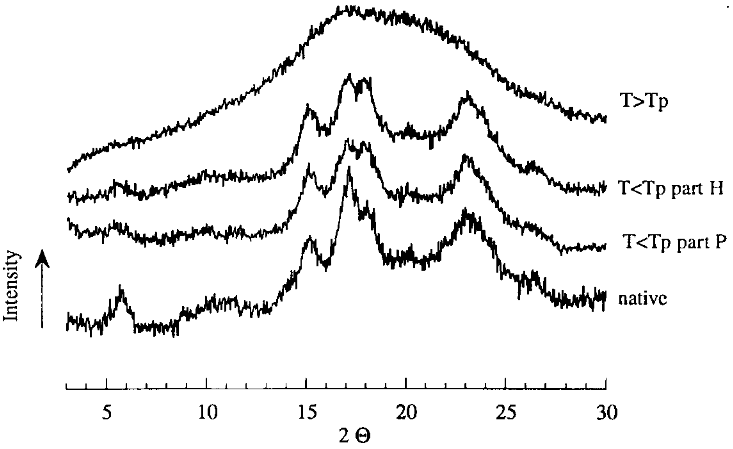

Fig. 4. X-ray diffractograms of native pea starch and pea starch processed in the Rheoplast® (MC = 30%, two temperatures and the same kinematic conditions).

(G for gelatinization) occurred at 66.8°C. As Donovan (1979) observed for potato starch, a second endotherm (M for melting) was observed when moisture content decreased (60–40%). The fraction of this first event, relative to the total transition enthalpy, decreased with decreasing moisture content. Peak G finally disappeared at MC = 35%. Although peak G temperature was constant, peak M shifted to a higher level when moisture content decreased. A change in the melting temperature of the last crystallite (T_f) relative to the volumic fraction of water was adjusted by the Flory–Huggins equation. The thermal transitions of smooth pea starch used in this work could be analyzed in the same way as those of starches from various botanical origins (Lelievre, 1973). For MC = 30 and 25%, only peak M was observed, characterized by a peak temperature (T_p) of 115 and 130°C, respectively.

3.3. Structural features of thermomechanically processed starch

Smooth pea starch was processed in the Rheoplast® according to various conditions favorable to one or another assumed mechanism. Above T_p, melting should be favored, whereas mechanical disintegration of starch granules should be predominant at lower temperatures. Processing temperatures, which take the influence of moisture content into account, were chosen on both sides of the peak temperature (T_p) of the melting endotherm determined by DSC. Treatments below and above T_p were, respectively, performed at 95 and 150°C for MC = 30% and at 110 and 150°C for MC = 25%. Rotation velocity was 50, 100 or 200 rpm, and residence times in the shearing zone were 15 and 30 s. Above T_p, samples were obtained with difficulty regardless of the moisture content chosen, and the experiments often had to be stopped after two or three cycles. In particular, no experiment could be carried out at 135°C for MC = 30%, owing to a lack of hydraulic power to unjam the central piston embedded in the molten starch. Increasing temperature to 150°C allowed us to perform these treatments by decreasing the viscosity of the molten starch (Vergnes & Villemaire, 1987). All results are shown in Table 1.

3.3.1. Processing at $T < T_p$ (experiments #1–3, #5–10)

These conditions allowed to observe intermediate levels of starch transformation.

Thick rods ($\varnothing \approx 16$ mm, $L \approx 50$ mm) were obtained. After immersion in deionized water, two radial zones could be distinguished: a peripheral powdery part (P) was in suspension, whereas the central translucent part (H) remained more homogeneous, without any significant swelling (Fig. 1b, I). These two radial zones were also distinguished by their rate of iodine sorption: part P sorbed iodine more quickly than part H. This difference in sorption kinetics was also observed between native starch and starch extruded on a pilot twin-screw extruder (MC = 30%, $T = 100$°C, SME = 1440 J g^{-1}). This variation could have been due to the general starch transformation level as well as to the compactness to the different parts of the sample (which were thus more or less accessible).

For MC = 30%, the elements in suspension (part P), when observed in light microscopy, corresponded to packed granules, and some elements with no apparent structure were strongly stained with Congo red (Fig. 2; (2)). These granules were not at the same stage of transformation: staining more or less pronounced, Maltese cross intact or modified, birefringence loss in the center of the granule. The crystalline content of samples was about 25–28%, with a significant decrease in B-type (4–5%) and stability of A-type crystallinity (20–24%). The B-type structure was still present, but difficult to quantify (Fig. 4). In visual detection, the lower threshold of the B-type in a blend of A-spherulites was previously found to be about 15% in relative value (Planchot, Colonna & Buleon, 1997b), which was roughly the level detected here. The gelatinization features in this part of the sample were similar: (i) residual gelatinization enthalpy of about 6.7 ± 0.5 J g^{-1} and (ii) a peak temperature and a temperature at the end

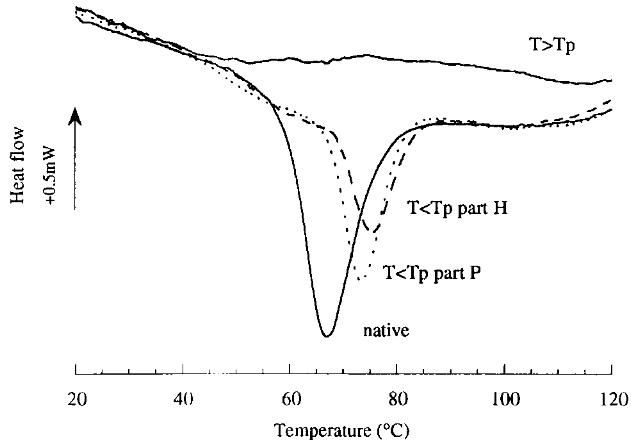

Fig. 5. DSC-thermograms of native pea starch and pea starch processed in the Rheoplast® (MC = 30%, two temperatures and the same kinematic conditions). Normalization at 20 mg of dry matter.

of this thermal event about 5–7°C higher than for native starch. The endotherm did not fit the pattern of native starch and was shifted at the highest temperatures (Fig. 5). The macromolecular structure was only slightly modified: values for the intrinsic viscosity of processed starch between 196 and 219 ml g^{-1}. Therefore, this part of the sample, which retained a powdery appearance, had different characteristics to those of native starch at the granular and crystalline levels.

Modifications in the granular structure of part H were analyzed by examining semi-thin sections in light microscopy (Fig. 2; (3)), in order to avoid any additional modifications due to grinding, whereas powdery samples were observed after dispersion in water. An initial impression of denser structure was only due to the sample preparation procedure. The granular structures remained, showing Congo red staining and an intact polarization cross. The population of birefringent granules was difficult to quantify: overall birefringence was overestimated owing to the thickness of the section. The density of the samples made it difficult to observe whether the polarization cross had been altered. Moreover, the magnification used, as well as the compactness of the sample, did not allow to determine whether processing had induced the bursting of some granules and thus a loss of granular content. The presence of intergranular cement, suggested by the behavior of sample zones after immersion in water, could not be confirmed. The crystalline structure was partially modified, with a crystallinity ratio after processing of 23–27% and no significant differences related to the mechanical processing. As for part P, the polymorphic composition had been modified: although the quantity of A-type crystals remained constant (20–24%), that of B-type crystals decreased sharply (3%) (Fig. 4). Residual gelatinization enthalpy decreased after processing to between 3.2 and 6.1 J g^{-1} (Fig. 5). This modification was accompanied by an increase in the peak temperature of gelatinization (T_{max} values between 73.8 and 75°C) and a decrease in peakwidth (ΔT values between 13.5 and 14.6°C) as compared to native starch (T_{max}, 66.8°C; ΔT, 19.6°C). The macromolecular structure was only slightly modified by the treatment (intrinsic viscosity between 200 and 220 ml g^{-1}).

When moisture content during processing was modified (MC = 25%), processing temperature was adjusted to take the temperature variation Tp into account. In this case, the degree of transformation achieved was similar to that obtained for a moisture content of 30%, regardless of the analytical method used (WAXS, DSC or intrinsic viscosity).

When processing was performed at 25°C (#5), some starch granules remained intact, or were fractured, or modified near the hilum (Fig. 2; (4)). The crystalline structure had partially disappeared, giving a residual crystallinity ratio of 18%. This loss of crystallinity was greater than that observed after treatment at 95°C for MC = 30%. Mechanical processing led to a decrease in residual gelatinization enthalpy, which was difficult to calculate precisely because of the peakwidth and the intensity of the signal. Macromolecular degradation was higher at this temperature, but lower than after extrusion ($[\eta] =$ 145 ml g^{-1} in previous conditions).

3.3.2. Processing at $T > T_p$ (experiments #4, #11–14 in Table 1)

The rods showed an irregular diameter because of slight expansion at the end of the transfer zone. The entire sample was translucent, and slices swelled after immersion in water while remaining cohesive. The quantity of starch lost in solution was negligible (0.2%).

When mechanical treatment was performed (#4, 11–13), slices were radially homogeneous (Fig. 1b; II). These samples, when observed by light microscopy, were composed of a mass of ghost granules stained with Congo red and zones with no apparent granular structure (Fig. 2; (5)). Birefringent granules remained in some minor zones of the section. Nevertheless, at this temperature, the vast majority of the granules had lost their radial organization. This disorganization was confirmed by WAXS and DSC. Typical amorphous diffractograms were obtained, and no residual endotherm remained (Figs. 4 and 5). Regardless of the mechanical processing used (rotation velocity, duration) and the moisture content during treatment, the starch was completely amorphous. Intrinsic viscosity decreased slightly (195–205 ml g^{-1}). When compared with the results of Vergnes et al. (1987) for corn starch processed in the Rheoplast® at low water content, the decrease in intrinsic viscosity relative to that of native starch was similar to theirs once mechanical processing was initiated.

However, when no mechanical processing was performed (#14), transformation was intermediate. Slices were then composed of powdery nodules dispersed in a translucent matrix without any preferential location (Fig. 1b; III). These nodules could not be separated after immersion in water, and slices kept their integrity despite slight swelling.

Intact starch granules were always observed, which were mainly packed but could sometimes be individualized within a matrix strongly stained with Congo red. Residual crystalline structures were observed, regardless of the method used (WAXS or DSC; crystallinity ratio = 14%; $\Delta H = 2.5\ \mathrm{J\ g^{-1}}$). No macromolecular degradation was observed.

3.4. Mechanism for obtaining a homogeneous molten phase

Treatments performed with the Rheoplast® modified the structural features of starch in the same way as extrusion, leading to a loss of granular and crystalline structures. Depending on barrel temperature, this destruction could be complete or intermediate. Thus, for $T > T_p$, melting was total, and this level of starch transformation was similar to that obtained at the end of an extruder, whereas samples obtained at $T < T_p$ were comparable to material being transformed along the screw in the proximity of an element restricting flow. In this case, the degree of transformation, at macroscopic and crystalline level (residual gelatinization enthalpy), was heterogeneous: the central part of the rod was more transformed than the peripheral part. This radial heterogeneity suggests different locations within the shearing zone in the Rheoplast®. Considering the high viscosity of the transformed material, the arrangement of particles was not modified by vertical transfer into the transfer zone, and the central part corresponded to material located close to the central piston (Villemaire, 1993). This heterogeneity was induced by the rotation of the central piston and not by water migration from hotter to colder parts, as suggested by the regular dispersion of powdery nodules within the rod slice when no shearing was associated with thermal processing. Furthermore, no significant difference in water content was noted in samples taken from the center and the peripheral part. Consequently, transformation was greater close to the moving, unheated part. Colonna et al. (1983), using a twin-screw extruder, observed a greater extent of transformation near the heated barrel. However, the exact location could not be clearly determined because of the high blending of material in the intermeshing zone within the extruder. Values for processing parameters in the Rheoplast® (temperature, 25–190°C; heating rate, $>50°\mathrm{C\ min^{-1}}$; shearing rate, $15–70\ \mathrm{s^{-1}}$) were in good agreement with those obtained in the extruder. The analogy between the extruder and the Rheoplast® could also be confirmed otherwise by comparing the transformation states obtained after processing with the Rheoplast® and along the screw of a twin-screw extruder.

Melting seemed mainly controlled by temperature: complete melting for $T > T_p$, partial melting for $T < T_p$. Although T_p was determined by DSC in conditions quite different from those encountered in the Rheoplast®. However shearing generated by the rotation of the central piston contributed to transformation, as indicated by a melting of the crystalline structure despite a barrel temperature below melting temperature (room temperature or $T_p - 20°\mathrm{C}$), in agreement with Zheng and Wang (1994). It also accelerated the phenomena as shown by comparing experiments at $T > T_p$: when no mechanical treatment was performed (#14), thermal transfers alone were insufficient to melt the whole material despite the temperature rise during limited duration.

At the granular level, for $T < T_p$, the modification of smooth pea starch began near the hilum through destruction of large distance order. This is often the first part of the native granule transformed by thermal processing when performed in excess of water or when moisture content is intermediate (Garcia, Colonna, Bouchet & Gallant, 1997; Kawabata, Takase, Miyoshi, Sawayama & Kimura, 1994). This central loss of birefringence was not accompanied by significant swelling, contrary to results for thermal processing performed with higher moisture contents (Zobel, 1984), and to the hypothetical mechanism proposed by Gomez and Aguilera (1984). As the processing was performed under pressure, the granules were compacted and swelling volume was limited. Under such moisture content conditions, water remained intragranular. No trace of shattering or surface erosion of granules was observed when heat was combined with mechanical treatment, but these mechanical effects were observed when processing at 25°C. Even for the highest level of transformation ($T > T_p$), forms of non-structured and deformed granules remained.

Crystalline structure was also partially modified for $T < T_p$. The crystallinity ratio was lower than for native starch, and polymorphic composition was modified. This global decrease was mainly due to the loss of B-type crystallinity after processing. Bogracheva, Morris, Ring and Hedley (1998) and Buleon, Gerard, Riekel, Vuong and Chanzy (1998a) have suggested that B-type crystallites are preferentially located in the center of smooth pea starch granules. The disappearance of B-type crystals after processing (as observed by WAXS) therefore increased the internal disorganization of the starch granule. The lower thermal stability of these crystals, in comparison with A-type crystals, could account for this phenomenon (Whittam, Noel & Ring, 1990). This partial melting of native crystals was also indicated by the decrease in gelatinization enthalpy values in excess of water observed after processing. Nevertheless, the shift in endotherms at higher temperatures could imply a structural reorganization related to this partial melting. For moisture contents of 25–30%, the temperature reached within the rod was higher than the glass transition temperature T_g (Biliaderis, Page, Maurice & Juliano, 1986; Bizot, Le Bail, Leroux, Davy, Roger & Buleon, 1997). The mobility of chain segments of the amorphous phase is therefore increased at the processing temperature (95°C), possibly allowing crystalline reorganization. However, thermal kinetics within the Rheoplast® were much higher ($\approx 100°\mathrm{C\ min^{-1}}$) than those generally associated with these sorts of reorganization ($3°\mathrm{C\ min^{-1}}$; Buleon, Le Bail,

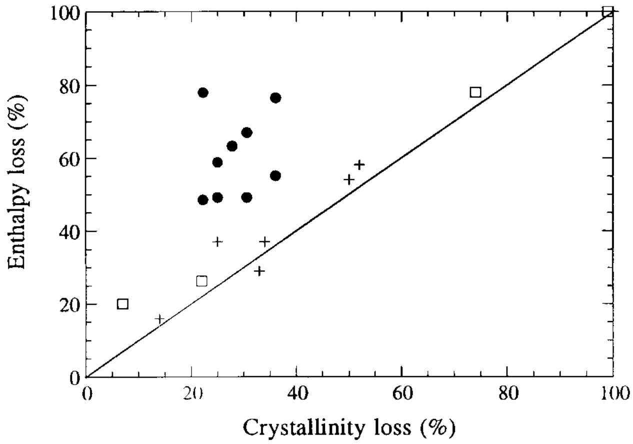

Fig. 6. Comparison between loss of crystallinity and gelatinization enthalpy. (●) Pea starch processed within the Rheoplast® at $T < T_p$. (□) Thermally processed cassava starch (MC = 35%) (Garcia, 1996), + Tapioca thermally processed in excess of water (Cooke & Gidley, 1992).

Colonna & Bizot, 1998b). Furthermore, no improvement in crystallinity or any polymorphic transition (B to A) was detectable by X-ray diffractometry (Fig. 4). Thus, in spite of chain mobility, crystal reorganization was unlikely, especially since the loss of A-type should have been equal to the quantity of B-type changed into A-type.

The modifications observed after thermomechanical processing were different from those encountered after thermal processing alone. The loss of gelatinization enthalpy, as determined after isolation and stabilization of the partially transformed sample, was not correlated with the loss of crystallinity (Fig. 6). Linear correlations between losses of gelatinization enthalpy and crystallinity have been reported by Garcia (1996) for cassava starch processed at a moisture content of 35% and by Cooke and Gidley (1992) for tapioca treated in excess of water. According to Jenkins and Donald (1998), starch crystallinity determined in situ decreases in a general way during gelatinization, even though the rate of crystallinity loss can vary. Samples processed within the Rheoplast® behaved differently. The loss of enthalpy was variable and clearly greater than that of crystallinity (a constant loss of 25%). The sample could not be modeled simply by a blend of native and completely amorphous granules, which was also suggested by the stable quantity of A-type crystals. Therefore no additive model was observed, as in the case of wheat starch damaged by mechanical action (Stevens & Elton, 1971). In our case, intermediate stages of transformation may have been present, so that the crystalline structure, strictly speaking, as well as the adjacent amorphous zone may have been modified. Considering the difference in the thermal kinetics imposed, processing with the Rheoplast® could have caused partial transformation of every starch granule, and not granule-by-granule melting. The crystalline structure was partially transformed, and B-type structures were more sensitive to this type of treatment. This partial melting was combined with a disorganization of the amorphous zone, which could explain differences observed between part H and P. Therefore the presence of intragranular cement (suggested by the cohesion of the part H) would not have resulted from greater disorganization of crystalline structures, at limits close to X-ray diffractometry detection sensitivity.

Regardless of the processing method used (temperature, shearing), macromolecular structure was only slightly modified. The loss of intrinsic viscosity was low compared to that observed after extrusion. After waxy corn starch extrusion, Willett, Millard and Jasberg (1997) found that molecular weight was reduced tenfold, corresponding to a two-fold decrease in intrinsic viscosity if the Mark–Houwink relation is applied using the exponent (0.29) obtained by Millard, Dintzis, Willett and Klavons (1997) for thermomechanically processed waxy corn starch. The range of variation in the intrinsic viscosity of smooth pea starch processed within the Rheoplast® was clearly narrower (5–15%), which could have been due to low levels of mechanical energy (60–370 J g^{-1}). This structural level seems to have been modified last, once a molten phase was obtained. Similarly, macromolecular degradation during extrusion was mainly observed in the conveying zone of the molten phase (Colonna et al., 1983). Finally, the higher macromolecular degradation observed at 25°C could have resulted from granule shattering. Shearing induced macromolecular degradation, as shown by the absence of a change of intrinsic viscosity when no mechanical processing was imposed.

4. Conclusions

The Rheoplast®, a pre-shearing rheometer, allows the transformation of starch by mechanical and thermal energy, as within extruders. Samples of intermediate transformation were obtained in this study to analyze the mechanism of obtaining a starchy molten phase.

Modification of starch on various structural scales was studied to determine which level is modified first by thermomechanical processing. Each analytical method used in this study contributed to evaluating the transformation, but none alone accounted for all the modifications. Obtaining a starchy molten phase therefore requires initial melting of the crystalline structure. This apparently begins near the hilum, without associated swelling, and is favored by disorganization of the amorphous zone. For processing temperatures which are clearly above T_g (more than 50°C), semi-crystalline starch granules behave like a deformable plastic material. Granules can then be deformed without loss of integrity. No single mechanical effect (erosion, shattering) was observed when processing associated heat and shearing, contrary to findings for synthetic polymeric particles extruded in a twin-screw extruder (Todd, 1993). The macromolecular structure is modified last and required the preliminary dispersion of the granular structure, possibly as soon as temperature and shearing velocity are sufficiently high. Nevertheless, this mechanism does not fit all observations, in particular the presence of an intergranular cement which could have contributed largely to rod cohesion. These issues need to be addressed using a more sensitive means of analyzing granular structure, particularly by electron microscopy, a method which has been used after extruder dead stop experiments showing damaged granules (Fletcher, McMaster, Richmond & Smith, 1984; Senouci & Smith, 1986).

Regardless of the mechanism of granule disruption involved, the use of the Rheoplast® under conditions favoring either mechanical or thermal energy inputs showed that temperature in particular is essential for obtaining a fully molten phase, whereas shearing decreases the time necessary for achieving it. The conversion of heat by friction or viscous dissipation seems more likely than direct granule erosion or fragmentation, although these phenomena cannot be discarded without further study. The respective shares of thermal and mechanical energy need to be determined to specify more accurately the mechanism of starch melting under actual processing conditions, for instance by setting up an energy balance of the shearing zone of the Rheoplast®.

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