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Isolation, Physicochemical Characterization and Application of Yam (*Dioscorea* spp.) Starch as Thickening and Gelling Agent

Yam starch of the species *Dioscorea alata* and *D. cayenensis-rotundata* was isolated, characterized by differential scanning calorimetry (DSC), X-ray diffraction, iodine titration, hot-stage microscopy and rheology, and compared to potato (*Solanum tuberosum*) and tapioca (*Manihot esculenta*) starch. The amylose content of yam starch was around 24% and tended to decrease during postharvest storage. Wide-angle X-ray diffraction showed a mixed A- and B-type crystalline packing. Differences between yam starches from different species and varieties were revealed by DSC. However, the largest differences between the different yam starches were found in terms of their rheological behavior. Yam starch shows an intermediate viscosity increase upon initial heating, but a stable viscosity during further thermal treatment in the Viscograph. Hot-stage microscopy showed a good preservation of the granular yam structure during heating, which is thought to be responsible for a rather high viscosity at low stress paired with a strong shear-thinning effect. The mechanical properties of yam starch gels suggest that the preservation of the granular integrity upon swelling limits amylose leaching, but that the aging behavior is primarily determined by the short-term changes of the amylose fraction. Yam starch has potential as thickening and gelling agent in food.

Keywords: Yam starch; Pasting; Viscosity behavior; Texturing agent

1 Introduction

Yam tubers present a tropical crop which is used as an energy-rich staple food mainly in West Africa where more than 90% of the world yam consumption is produced [1]. The dry matter content of yam tubers varies between 20 and 40% which in turn consists of 60–80% of starch depending on the variety, the duration and the condition of postharvest storage. One particularity of yam is the great botanical variety, *D. cayenensis-rotundata* and *D. alata* being the mostly cultivated species with a large number of varieties [2]. Yam tubers may be stored for several months, but sprouting is accompanied by considerable dry matter and water losses. Gibberellic acid (GA₃) application and regular desprouting are effective treatments to reduce postharvest losses of yam [3].

Starch belongs to the most important thickening and gelling agents in food. Compared to potato and tapioca starch, the two most commercialized tuber starches for

food application, the utilization of yam starch is limited to local production and application of yam flour. However, more attention has been paid to yam starch in the past years as manifested by an increasing number of publications on this topic [4–6]. A comprehensive review of the properties of yam starch is given by Hoover [7].

Rolland-Sabaté et al. [8] classified yam starches into three groups, the first class consisting of *D. alata* and *D. cayenensis-rotundata* varieties with large starch granules, high amylose contents, high intrinsic and apparent viscosities and low gelatinization enthalpies, a second class representing *D. esculenta* varieties, which have small granules, low intrinsic and apparent viscosities and high gelatinization enthalpies, and the third class including *D. dumetorum* varieties being close to the second class but showing A-type crystallinity by wide-angle X-ray diffractometry. Native tropical tuber starches can be divided into A- and B-type starches, the commercially important yam starches belonging to the latter type [9]. Gunaratne and Hoover [10] found that yam starch is little susceptible towards porcine pancreatic α -amylase compared to other tuber starches. Differences in granule size and the presence of α (1→6) branch points in the crystalline regions of A-type starches are responsible for this phenomenon.

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The present investigation aimed at characterizing the physicochemical properties of yam starch isolated from different yam species and varieties. Yam tubers of the species *D. alata* and of the *D. cayenensis-rotundata* complex were included in the study, since they belong to the most important cultivated yam species in West Africa. The *D. cayenensis-rotundata* complex includes two species that can not be distinctly separated with morphological and molecular analysis [11]. Freshly harvested and stored yam tubers, which had been either treated with gibberellic acid or regularly desprouted were investigated. The starch of the proximal and the distal part of the tuber was characterized, because in the monocotyledonous yam tuber a compositional gradient exists along the longitudinal axis, most probably caused by growth physiology [12]. The amylose content was determined by iodine titration and the supramolecular starch structures were characterized by differential scanning calorimetry (DSC) and X-ray diffraction. The morphological changes upon swelling of yam starch were followed by hot-stage light microscopy. Emphasis was placed on the rheological characterization of low concentration yam starch dispersions and high concentration yam starch gels that served as food model systems to assess the properties of these starches as thickening and gelling agents. Commercial potato and tapioca starch were included in the study for comparative purpose.

2 Experimental

2.1 Materials

Yam tubers of the species *D. alata*, varieties Bètè bètè and Florido, and *D. cayenensis-rotundata*, variety Kren-glè, were obtained immediately after harvest from the southern part of the Ivory Coast and used either fresh or after a storage period of three months in the Ivory Coast on traditional yam barns. During postharvest storage the yam tubers were either not treated (control), with gibberellic acid (GA₃) treated or desprouted biweekly as described by Tschannen *et al.* [3]. GA₃ was dispersed in cassava pastes (600 mg GA₃/tuber) and applied on the truncated proximal tuber parts at the beginning of the storage period. Freshly harvested and postharvest stored tubers were transferred by air-freight to our laboratory where they were kept at conditions of minimal physiological activity, i.e. at a temperature of 17°C and 70% relative air humidity.

Commercial native potato starch and native tapioca starch were obtained from Blattmann & Co. AG, Wädenswil, Switzerland and Avebe, Veendam, Netherlands, respectively.

2.2 Extraction of yam starch

Yam starch was extracted by a method adapted from procedures described in the literature [5, 13]. For some experiments, starch was extracted from the proximal and the distal half of the tuber, respectively. Batch size varied between 1 and 5 kg and the number of tubers per extraction batch varied between one and four. The tubers were peeled manually and grated (Anliker vegetable cutter GSM I/77, Brunner Maschinenfabrik und Giesserei, Kloten, Switzerland). The small pieces were incubated in excess 0.05 M NaOH solution for 4 h and milled with a corundum colloid mill (Type MZ-80/R, Fryma-Maschinen AG, Rheinfelden, Switzerland) in a circulating mode of operation. The gap width of the mill was reduced continuously from 3.0 to 0.4 mm. The milling condition (gap size) was controlled by light microscopy to ascertain that the cells were disrupted but that the starch granules were not damaged. After milling, the slurry was incubated at 17°C for 20 h to macerate the cell walls and to settle the starch fraction. The pH was kept between 8 and 9 during this period. The supernatant was discarded and the extract was filtered through sieves with decreasing mesh size (0.5, 0.25 and 0.1 mm) to separate the cell wall material from the starch fraction. The final sieve residue was rinsed several times with deionized water until a neutral pH was reached. The starch suspension was decanted and the starch was dried in thin layers in a convection oven at 30°C until weight constancy.

The dry matter content of yam tissue was determined by weighing 5 g of peeled and finely cut yam tissue into cylindrical steel pans (diameter 62 mm, height 25 mm) followed by drying in a vacuum oven (M. Chopin & Co., Boulogne, France) for 22 h at 70°C, 0.9 bar pressure and a percolation of dried air (silicagel/zeolite) at a flow rate of 1.5 L/min. Measurements were carried out with two to three replicates. The moisture content of the extracted and of commercial starches was determined gravimetrically in an infrared-dryer at 120°C for 10 min in duplicate (LP 16, Mettler-Toledo, Greifensee, Switzerland).

2.3 Physicochemical characterization of yam starches

2.3.1 Purity and amylose content of isolated starches

The total starch content was determined enzymatically [14, 15]. Isolated starch (20 mg) was weighed into 50 mL centrifuge tubes and solubilized with 6 mL 2 M KOH. After neutralization with HCl the starch was hydrolyzed to D-glucose by amyloglucosidase. The D-glucose

content was determined with hexokinase/glucose-6-phosphate dehydrogenase. Samples were tested in duplicate.

The amylose content of the extracted yam starch was calculated from the measured iodine binding capacity (IBC). Starch dispersions at a concentration of 1 g/100 g dispersion were prepared by heating at 95°C for 10 min, followed by cooling to 25°C. The IBC was determined with amperometric iodine titration as described by Szejtli [16] with a Metrohm titrator (Polarizer E585, Potentiograph E576, Dosimat 655, Metrohm, Herisau, Switzerland). A 30 g sample containing 100 mg starch, 1 mL 1 M HCl and water was titrated with 0.005 M iodine solution at a titration rate of 0.25 mL/min. Polarization voltage of the platinum electrode was 140 mV and the attenuation was set at 5 μ A. Deionized water (29 mL) with 1 mL 1 M HCl served as a blank and was subtracted from the starch specimen values. The titration curve was plotted on scale paper and evaluated graphically. The IBC was calculated with Equation (1), where I_b is the amount of bound iodine and S_{tot} the amount of starch in the titration vessel. The amylose content of the sample was calculated assuming an IBC of 19.5% for pure amylose [17]. At least three determinations per extraction batch were carried out.

$$IBC = 100 \cdot I_b / S_{tot} \quad [\text{mg iodine}/100 \text{ mg starch}] \quad (1)$$

2.3.2 Wide-angle X-ray diffraction

The crystalline structures of starch were characterized by wide-angle X-ray diffraction. The starches were kept over water for 90 min in a closed vessel to reach a moisture content of 11–14 g/100 g moist sample, pressed into pills (thickness 1–2 mm, diameter 13 mm) and mounted on holders in a powder diffractometer (Siemens Kristalloflex D500, Karlsruhe, Germany). A CuK_α radiation (1.54 Å) at 35 mA and 40 kV, and a divergence slit of 2 mm and a receiving slit of 1 degree were selected for the measurements at room temperature. The scattering angle range (2θ) for registration of the relative intensity was 4–30° with a scintillation counter at a scanning speed of 0.02°/min.

2.3.3 Differential scanning calorimetry (DSC)

Native starch suspensions (30 g dry starch/100 g suspension) were measured with differential scanning calorimetry (Thermal Analyst 2000, DSC 2910, TA Instruments, New Castle, UK). A first run was carried out with native starch suspensions within 30 min after preparation of the suspension, the second run was carried out after 7–9 days of aging in the sealed pans. An empty pan was used as reference. The melting enthalpy and the melting tem-

perature were calibrated with indium. The starch suspension (40 mg) was weighed into DSC steel pans (Perkin Elmer Ltd., Norwalk, CT, USA) and heated from 4 to 180°C with a heating rate of 10°C/min. The peak melting temperature (T_{Peak}) and the melting enthalpy (ΔH) were evaluated. At least three determinations per extraction batch were carried out.

2.3.4 Hot-stage light microscopy

The morphological changes of starch granules upon heating were followed by heating starch suspensions (0.5 or 2 g starch/100 g) in a sealed aluminum sample chamber with an optical window on a hot stage (LTS 350, Linkam, Tadworth, UK) under the light microscope (Axioscope 2 mot, Zeiss, Feldbach, Switzerland) in the polarization mode or in the differential interference contrast mode. The temperature was increased at a rate of 10°C/min. Micrographs were taken at regular intervals with a camera (Pixelink PL-A662) mounted on the microscope. For temperature acquisition the probe of the thermocouple was put into the sample.

2.4 Applications of starch as thickening and gelling agent

The properties of yam starch as thickening and gelling agent were studied with different rheological methods. Pasting of aqueous starch suspensions upon heating was followed with the Brabender Viscograph. In addition, the flow behavior of starch dispersions was studied. Finally, the mechanical properties of starch gels were assessed with compression tests.

2.4.1 Low concentration aqueous starch systems

The pasting properties of starch suspensions at a concentration of 5.4 g dry starch/100 g were assessed by a Viscograph (Viscograph E, Brabender OHG, Duisburg, Germany). The samples were heated from 30 to 95°C with a hold time of 30 min followed by cooling to 50°C with another 30 min hold time. The heating and cooling rate were set at 1.5°C/min. The viscograms were recorded in duplicate and because of congruency one is shown for every sample.

Furthermore, the rheological properties of starch dispersions were characterized by steady-shear rheometry. The samples were prepared by heating suspensions of 2 g dry starch/100 g to 95°C in a water bath with a hold time of 30 min under constant stirring. The amount of evaporated water was determined by weighing and replaced. The

starch dispersions were transferred into closed vessels and kept at 25°C. Within two hours after preparation the rheological properties were measured with a controlled-stress rheometer (CS 100, Carri-Med Ltd., Surrey, UK) equipped with a cone-plate geometry (diameter 6 cm, angle 1 degree 59 min). The flow behavior was measured in a shear stress range of 0–150 N/m² at 25°C and the upward curve was registered within 1.5 min in triplicate. The experimental data were modeled with the Cross equation (Eq. 2), where $\dot{\gamma}$ is the shear rate and η_0 and η_∞ the viscosities at low and high shear stresses, respectively. The dimension of the constant K is time whereas the constant m is dimensionless and describes the power-law region at intermediate shear rates.

$$(\eta - \eta_\infty) / (\eta_0 - \eta_\infty) = 1 / (1 + (K \cdot \dot{\gamma})^m) \quad (2)$$

2.4.2 Starch gels

Starch gels at a concentration of 30 g dry starch/100 g gel were prepared as described by Hug-Iten et al. [18]. This method consists in stirring the main portion of native starch into a pregelatinized starch dispersion (2 g/100 g) to avoid the sedimentation of starch. The starch suspension was filled into cylindrical brass moulds (diameter 30 mm, height 20 mm). The moulds were sealed and heated in a convection oven during 1 h at 98°C. The gels were cooled without opening the moulds by immersion in cold water for 10 min and aged in the mould at 17°C. The gels were characterized by uniaxial compression directly after preparation and after an aging period of 2–14 d. Gels were compressed 12 mm (60%) between two plates in an universal testing machine (Z010, Zwick GmbH & Co., Ulm, Germany) at a crosshead speed of 50 mm/min with three repetitions. To prevent barreling of the gels upon deformation the plates were greased with paraffin. From the force-deformation curves the modulus of deformability (E_D) between 5 and 10% deformation and the breaking stress was evaluated as described by Hug-Iten et al. [18]. The breaking stress (σ_b) was calculated by transforming the measured force into stress by taking into account the increase of the cross-sectional area of the gel during biaxial deformation [19].

3 Results and Discussion

3.1 Isolation and characterization of yam starch

The dry matter content of the analyzed yam tubers is shown in Tab. 1. A higher dry matter content was found for the varieties Krenglè and Bètè bètè compared to Florido. However, in general it is found that the dry matter content of *D. alata* varieties is clearly lower than that of

Tab. 1. Dry matter content of fresh and stored yam tubers used for starch extraction. Averages (\bar{x}) and ranges (R) of N extraction batches (with total number of tubers in parentheses).

Sample	N	Dry matter content [g/100 g wb]	
		\bar{x}	R
Fresh yam tubers			
<i>D. alata</i>			
Bètè bètè, whole tuber	1 (3)	31.9	9.5
Florido, whole tuber	2 (2)	23.4	9.6
Florido, proximal part	3 (11)	28.5	3.0
Florido, distal part	3 (11)	21.8	5.9
<i>D. cayenensis-rotundata</i>			
Krenglè, whole tuber	2 (7)	34.6	17.6
Three months stored yam tubers			
<i>D. alata</i>			
Florido, whole tuber, non-treated	1 (2)	25.0	6.4
Florido, whole tuber, GA ₃ -treated	1 (1)	22.7	6.7
Florido, whole tuber, desprouted	1 (1)	25.4	8.6

D. cayenensis-rotundata. The dry matter content was higher in the proximal than that in the distal part of the tubers. This confirms that large differences may not only exist between different species, but also between tubers of the same variety and within one tuber. The yield of starch was between 80 and 150 g starch/kg fresh (peeled) yam, and purity between 97 and 100 g starch/100 g dry extract was obtained.

The amylose content of yam starches as determined by amperometric iodine titration is presented in Tab. 2. Significant differences in the amylose content were found neither between yam varieties nor between the proximal and distal part of the tuber. A trend towards slightly lower amylose contents was found upon storage of Florido tubers, but no differences were seen between different postharvest treatments.

The amylose content of the investigated yam starches is in good agreement with the literature [5, 10]. The amylose content of yam starches is comparable to that of potato and tapioca starch, the values for potato starch being slightly higher than that of tapioca starch. The finding that the amylose content of Florido tubers tends to decrease upon storage could be related to the observation that the total starch content decreases [20]. It is likely that the synthesis pathway of amylose and amylase activity may be responsible for changes in the amylose content [21], which for yam starch should be subject to further investigations.

Tab. 2. Amylose content of yam starches. Extraction of starch from fresh and stored yam tubers. Averages (\bar{x}) and ranges (R) of N extraction batches (with total number of tubers in parentheses).

Sample	N	Amylose content [g/100 g dry starch]	
		\bar{x}	R
Fresh yam tubers			
<i>D. alata</i>			
Bètè bètè, whole tuber	1 (3)	23.4	2.9
Florido, whole tuber	2 (2)	25.4	1.5
Florido, proximal part	3 (11)	24.1	3.2
Florido, distal part	3 (11)	24.5	2.5
<i>D. cayenensis-rotundata</i>			
Krenglè	2 (7)	25.6	1.2
Three month stored yam tubers			
<i>D. alata</i>			
Florido, whole tuber, non-treated	1 (2)	22.6	1.5
Florido, whole tuber, GA ₃ -treated	1 (1)	22.3	1.1
Florido, whole tuber, desprouted	1 (1)	22.5	1.8
Potato		24.5	1.8
Tapioca		22.3	0.7

The X-ray diffraction patterns of starch allow a characterization of the crystal packing in the native granules. The diffractograms of the extracted yam starches in comparison to commercial potato and tapioca starch are presented in Fig. 1. The diffractogram of potato starch showed pronounced peaks at 5.7°, 17° and 22–24° 2 θ angle which correspond to the expected B-type pattern. Tapioca starch presented reflections at 15.1°, 17.15° and 23° 2 θ angle which correspond to the expected A-type pattern. Yam starches showed a weak peak at 5.7° and 15.1°, and a pronounced peak at 17.1° and 23° 2 θ angle. These reflection values are interpreted as intermediate diffraction pattern between A- and B-type, which stands in contrast to literature [7, 9], where starches of *D. cayenensis*, *D. rotundata* and *D. alata* starches were described to show a B-type pattern.

The melting of native starch crystals in presence of water was followed by DSC and the increase of starch polymer order upon aging of gelatinized starch was assessed. As shown in Fig. 2 A, the native starches present an endothermic phase transition between 63 and 110°C, which reflects the loss of crystalline and double helical order upon starch granule swelling. The peak temperatures and the enthalpies of melting are summarized in Tab. 3. The

Tab. 3. Peak temperature (T_{Peak}) and enthalpy (ΔH) of endothermic phase transitions of yam starches at concentrations of 30 g dry starch/100 g suspension. Extraction of starch from fresh and stored yam tubers. Averages (\bar{x}) and ranges (R) of N extraction batches (with total number of tubers in parentheses).

Sample	N	T_{Peak} [°C]		ΔH [J/g db]	
		\bar{x}	R	\bar{x}	R
First run (native starch)					
<i>D. alata</i> , fresh					
Bètè bètè	1 (3)	81.6 (0.5)		19.9 (1.8)	
Florido, whole tuber	2 (2)	78.4 (1.5)		23.2 (6.2)	
Florido, proximal part	3 (11)	77.8 (1.1)		22.0 (4.7)	
Florido, distal part	3 (11)	78.3 (0.8)		21.3 (3.0)	
<i>D. cayenensis-rotundata</i> , fresh					
Krenglè	2 (7)	75.0 (1.6)		21.3 (1.6)	
<i>D. alata</i> , stored for 3 months					
Florido, non-treated	1 (2)	78.6 (0.5)		23.3 (1.1)	
Florido, GA ₃ -treated	1 (1)	79.2 (0.3)		24.0 (4.6)	
Florido, desprouted	1 (1)	78.2 (0.3)		23.4 (4.4)	
Potato		68.0 (1.9)		24.1 (4.5)	
Tapioca		75.3 (0.9)		18.8 (2.0)	
Second run after an ageing period of 7–9 d					
<i>D. alata</i> , fresh					
Bètè bètè	1 (3)	70.9 (0.8)		12.3 (2.1)	
Florido, whole tuber	2 (2)	72.6 (5.1)		13.5 (5.8)	
Florido, proximal part	3 (11)	72.1 (3.2)		12.1 (4.3)	
Florido, distal part	3 (11)	72.8 (1.7)		11.0 (2.0)	
<i>D. cayenensis-rotundata</i> , fresh					
Krenglè	2 (7)	70.2 (1.7)		10.9 (2.3)	
<i>D. alata</i> , stored for 3 months					
Florido, non-treated	1 (2)	72.3 (0.5)		12.8 (1.4)	
Florido, GA ₃ -treated	1 (1)	73.1 (0.9)		13.6 (7.3)	
Florido, desprouted	1 (1)	73.2 (0.4)		11.9 (5.1)	
Potato		68.7 (2.1)		12.0 (3.2)	
Tapioca		66.6 (1.8)		2.0 (0.4)	

peak temperature varied between 75.0–81.6°C and was highest for variety Bètè bètè followed by Florido and Krenglè, but no differences between yam varieties were found regarding the transition enthalpies. Likewise, no differences were found between starches extracted from stored and fresh tubers. The comparison between yam and other tuber starches showed that tapioca starch is similar to yam starch, while the melting of potato starch initiated at lower temperatures (68°C). The melting enthalpies of potato and tapioca starch were at the upper and lower end of the values found for yam starches.

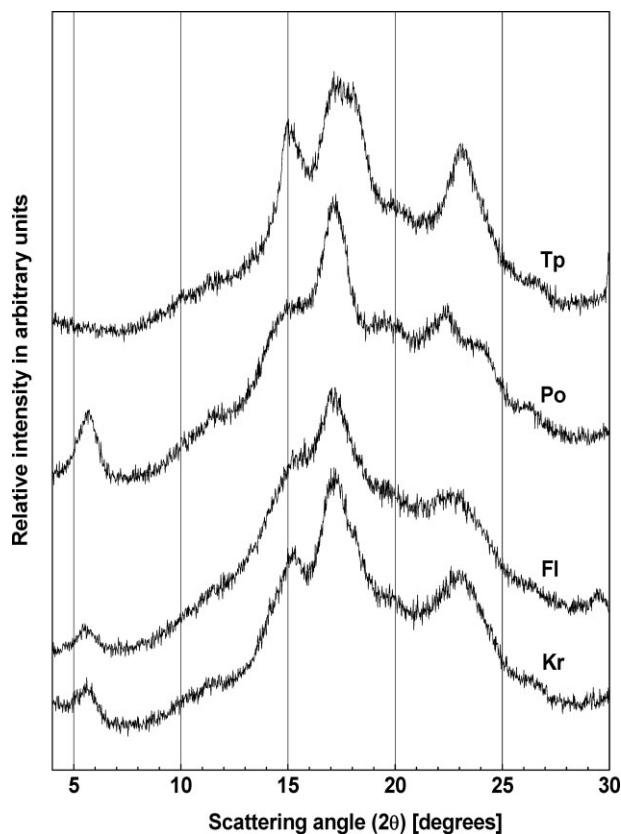


Fig. 1. Wide-angle X-ray diffractograms of yam (varieties Florido (Fl) and Krenglè (Kr)), potato (Po) and tapioca (Tp) starch.

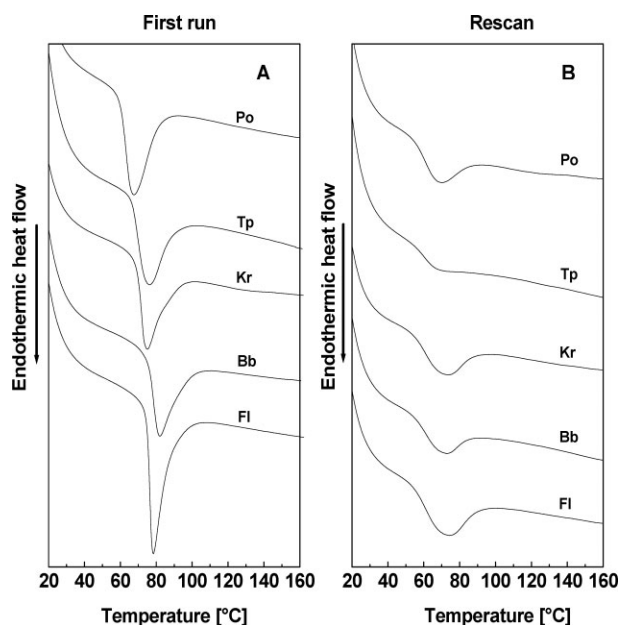


Fig. 2. DSC thermograms of yam (varieties Florido (Fl), Bètè bètè (Bb) and Krenglè (Kr)), potato (Po) and tapioca (Tp) starch suspensions (30 g dry starch/100 g suspension), the rescan was after 7–9 d of aging.

An immediate rescan of the samples revealed no transition (results not shown). However, as shown in Fig. 2 B and Tab. 3, a rescan of the samples after an aging period of 7–9 d revealed again an endothermic transition with a peak temperature at $72 \pm 1^\circ\text{C}$ for yam starches. This transition corresponds to the melting of newly formed ordered starch structures, primarily involving amylopectin, this phenomenon is also referred to as retrogradation. The melting enthalpies of this transition were half of those of the native starches. No important differences were found between the different yam starches. A noticeable difference between yam and potato starch is that the latter presented the same melting temperature for native and for retrograded starch. Tapioca starch on the other hand, presented retrogradation enthalpies that were six times lower than that of the other tuber starches, which is in agreement with the literature [22].

The DSC measurements were complemented with light microscopy in the polarization mode to follow the changes of yam starch during heating. Fig. 3 shows the DSC thermogram and micrographs of the variety Krenglè. Note that the heating rate was the same for the two techniques ($10^\circ\text{C}/\text{min}$). The concentration was different for DSC and hot-stage microscopy (30 and 2 g/100 g suspension), but in both cases starch was heated at excess water conditions where the melting temperature is independent of starch concentration. The endothermic DSC peak coincided with the progressive loss of starch birefringence. However, the disappearance of birefringence did not occur simultaneously for all granules, and at the peak temperature of 75°C most granules had lost their birefringence. At 90°C , when melting was completed, no birefringence could be detected, but the granular structure of the granules was still preserved, although in a swollen state.

The morphological changes of yam starch of the variety Krenglè and Florido were followed by hot-stage microscopy in comparison to potato starch and selected micrographs are shown in Fig. 4. In general the granule size distribution of yam starches was more uniform than that of potato starch [23]. Swelling of yam starch granules occurred at higher temperatures compared to potato starch, which is in agreement with the DSC measurements. A noticeable difference between yam and potato starch is the extent of swelling, which was clearly less pronounced for the two yam starches. The high swelling power of potato starch is in part explained by its phosphate content. Florido starch granules preserved their triangular shape even after swelling, whereas Krenglè starch granules presented a more spherical morphology. A further particularity of swollen yam starch is the wrinkled structure at one edge of the granule which is more pronounced for the variety Florido. Similar morphological

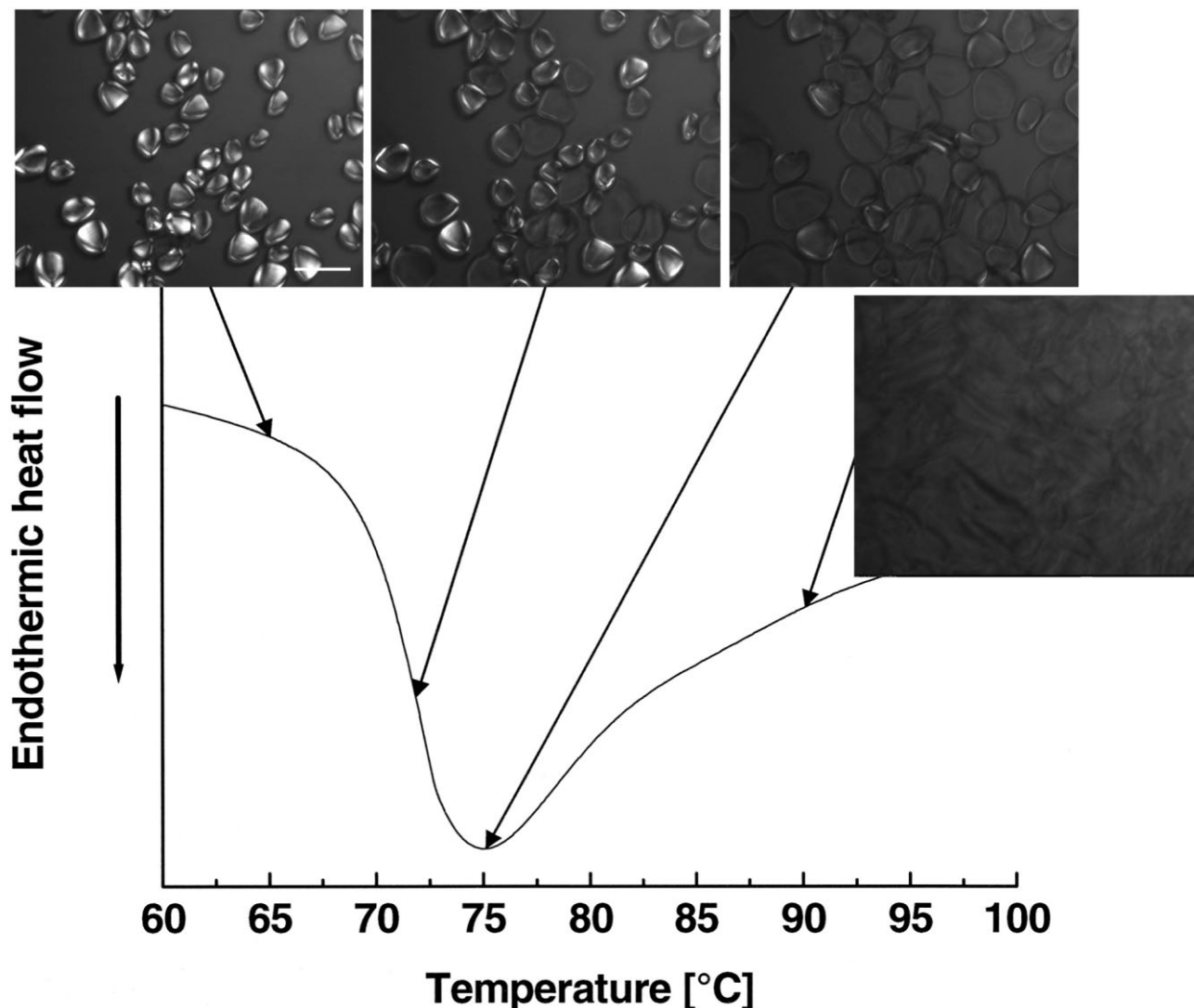


Fig. 3. DSC thermogram of a yam starch suspension (30 g dry starch/100 g suspension) compared to changes in the granule birefringence during gelatinization of the same yam variety (Krenglè) observed with polarization microscopy at a hot stage (white bar = 50 μm).

changes of starch granules were detected during boiling of yam tissue when intact starch granules were released from damaged cells into the cooking water [24].

3.2 Performance of yam starch as texturing agent

The pasting behavior of the investigated yam starches as assessed with a Viscograph is shown in Fig. 5. Yam starches presented a higher gelatinization temperature compared to tapioca and potato starch, and in terms of peak viscosity, yam starches took an intermediate position between potato and tapioca starch, which showed very high

and low viscosities, respectively. The peak viscosity of yam starches decreased in the order Krenglè > Bètè bètè > Florido. The yam starches did not show a strong viscosity decrease upon further heating as it is the case for potato starch. Krenglè even presented a marked viscosity increase upon cooling to 50°C which led to the highest final viscosity (at 50°C) followed by starch from Bètè bètè, potato and Florido with similar viscosities.

Similar pasting behaviors of starches from *D. alata* and *D. rotundata* were found by Alves et al. [4] and Farhat et al. [5]. In contrast to the present results, they found smaller differences in the pasting pattern between cassava and yam starch. The delayed viscosity increase for yam star-

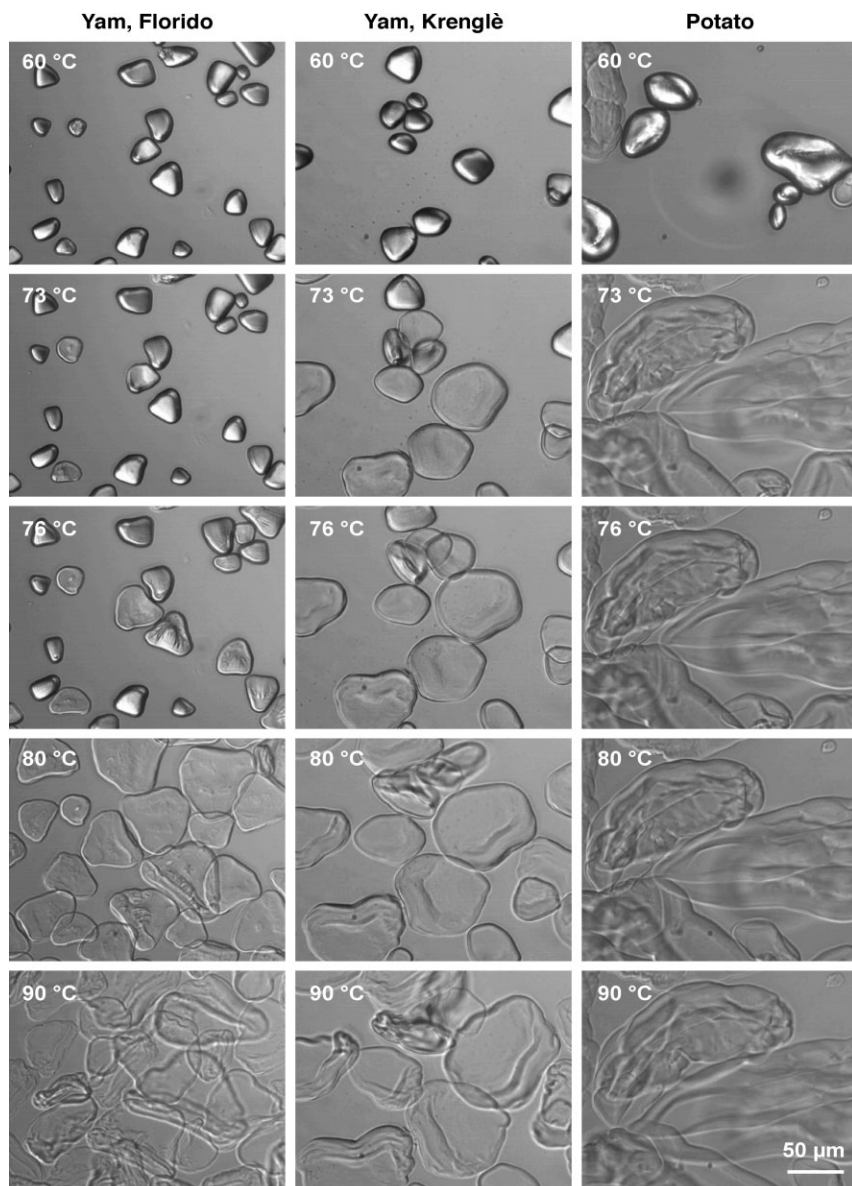


Fig. 4. Starch gelatinization followed with hot stage light microscopy in the differential interference contrast (DIC) mode. Yam (varieties Florido (left column) and Krenglè (middle column)) and potato starch (right column) are compared at concentrations of 0.5 g dry starch/100 g suspension.

ches coincided with high peak melting temperatures as measured with DSC and delayed swelling as revealed by hot-stage microscopy. The fact that yam starch dispersions can maintain their viscosity during heating and stirring at 95°C is most probably related to the extent of granule swelling as could be shown by hot-stage microscopy. Starches with high swelling power, such as potato starch are known to be susceptible towards granule disintegration upon thermomechanical processing. The pronounced viscosity increase of Krenglè starch upon cooling compared to Bètè bètè and Florido could be due to a high structural rigidity of the swollen granules and/or to an increased aggregation rate of amylose, although yam starches tend to release less amylose than potato starch at 90°C [10].

In addition, low concentration starch dispersions (2 g dry starch/100 g dispersion) were characterized by rotational viscosimetry. Viscosity curves of starch dispersions measured at 25°C are presented in Fig. 6. All starch dispersions showed a shear-thinning (pseudo-plastic) behavior as it is typical for polymer dispersions. The general shape of the curve revealed a constant viscosity value at very low shear stresses, and a second asymptotic viscosity value at very high shear stresses. The intermediate region of the viscosity curve was characterized by a more or less pronounced decrease of viscosity, also referred to as the power-law region [25]. Tapioca starch dispersions showed a much lower viscosity than all other investigated starches, which is in agreement with the results of the Brabender Viscograph. The flow curves of yam and

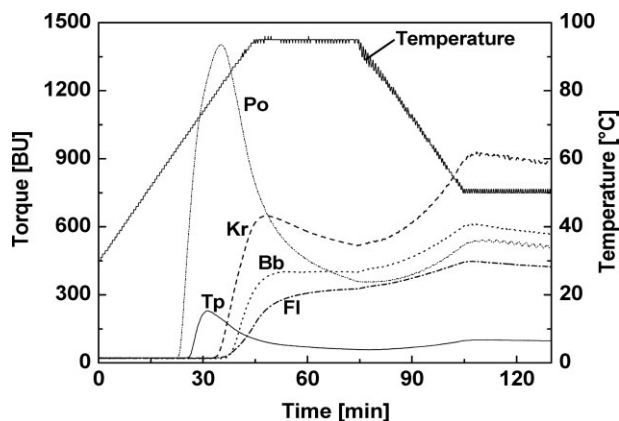


Fig. 5. Brabender viscosograms of yam (varieties Florido (FI), Bètè bètè (Bb) and Krenglè (Kr)), potato (Po) and tapioca (Tp) starch pastes (5.4 g dry starch/100 g paste).

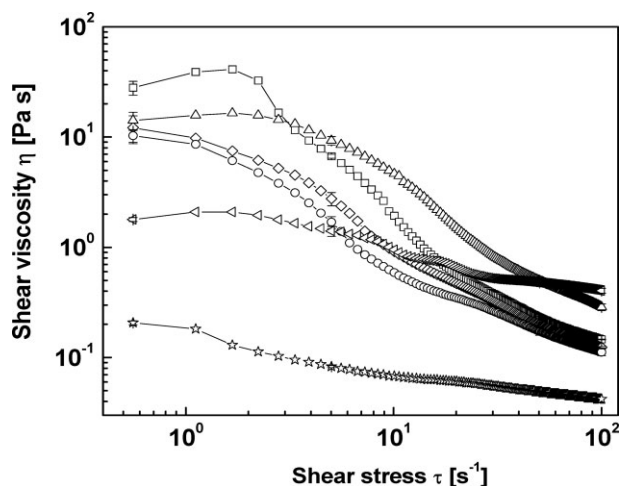


Fig. 6. Viscosity curves of yam (varieties Florido (□) and Krenglè (Δ)), potato (▷) and tapioca (☆) starch dispersions (2 g dry starch/100 g dispersion). From Florido starch was extracted from proximal (◇) and distal tuber parts (○) separately.

potato starches covered a similar viscosity range, but large differences were found in the flow behavior, as evaluated by the Cross model, Tab. 4. Yam starches presented high η_0 viscosities compared to potato starch. For Florido, the η_0 viscosity for starch extracted from the whole tuber was higher than that extracted from the proximal and distal parts. In contrast to potato starch, yam starches presented a much stronger shear-thinning effect as indicated by the low values of the constant m of the Cross model. As the shear stress increased, the viscosity curves converged and the η_∞ viscosities of potato and yam starches were in the same order of magnitude.

The flow behavior of starch dispersions is primarily related to the volume fraction occupied by the swollen granules which act as fillers, by extent of shear-induced granule disintegration and by the amylose concentration in the continuous phase [26]. No explanation is found for the differences between starch from the proximal and distal part of the tuber. However, it has to be noted that for this particular experiment, the starch was extracted from the two extremities of the tuber and the central part was discarded. The large differences in the flow behavior of tuber starches most likely reflect differences in the extent of granule swelling and granule rigidity. In terms of texture, the flow behavior of yam starch dispersions can be interpreted as having a good thickening effect (high viscosity at low shear stress) combined with a non-slimy mouth feel (strong shear thinning) [27]. On the other hand, hydrocolloid solutions with low shear thinning such as potato starch are perceived as slimy (also known as long texture). In contrast, tapioca starch is characterized by a low thickening power.

Finally, the mechanical properties of concentrated starch gels (30 g starch/100 g) upon aging were measured. The modulus of deformability (E_D) and the breaking stress (s_b) of yam and potato starch gels are presented in Fig. 7. E_D

Tab. 4. Cross model fit of viscosity curves of yam starch at concentrations of 2 g dry starch/100 g dispersion (three replicates of one extraction batch, std = standard deviation, R^2 = coefficient of determination).

Starch	η_0 [Pa·s]		η_∞ [Pa·s]		K [s]		m [-]		R^2		std	
	\bar{x}	(std)	\bar{x}	(std)	\bar{x}	(std)	\bar{x}	(std)	\bar{x}	(std)	\bar{x}	(std)
<i>D. alata</i>												
Florido, whole tuber	64.03	(±6.8)	0.097	(±0.004)	23.50	(±2.6)	0.73	(±0.007)	0.996	(±0.002)	17.80	(±4.5)
Florido, proximal	16.34	(±3.3)	0.074	(±0.002)	5.52	(±1.0)	0.68	(±0.011)	0.999	(±0.001)	9.47	(±2.6)
Florido, distal	13.44	(±1.8)	0.088	(±0.005)	4.55	(±0.6)	0.73	(±0.003)	0.998	(±0.000)	17.12	(±0.8)
<i>D. cayenensis-rotundata</i>												
Krenglè, whole tuber	21.91	(±2.6)	0.156	(±0.030)	2.06	(±0.5)	0.72	(±0.037)	0.994	(±0.002)	15.29	(±3.5)
Potato	2.26	(±0.1)	0.370	(±0.033)	0.22	(±0.1)	0.94	(±0.113)	0.981	(±0.010)	15.13	(±2.6)

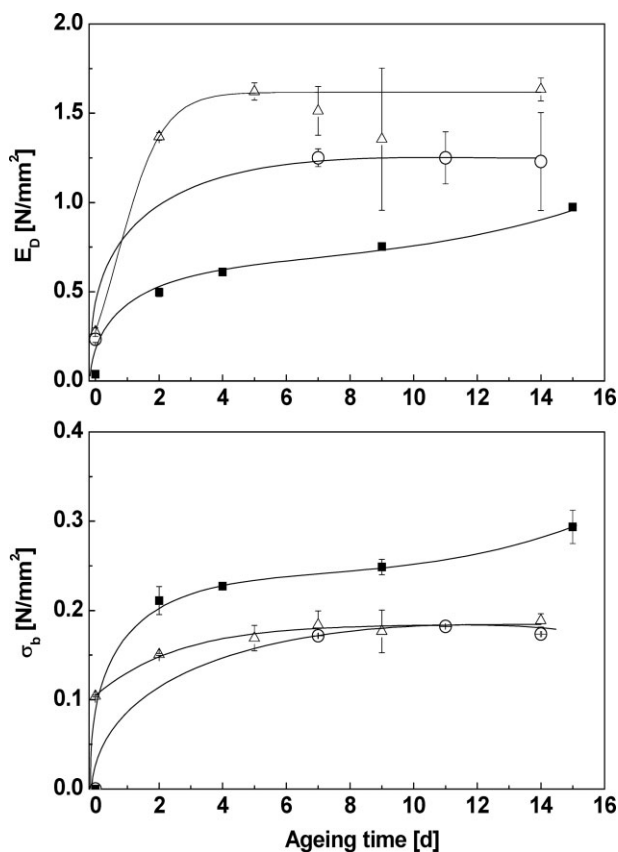


Fig. 7. Modulus of deformability (E_D) and breaking stress (σ_b) as a function of aging time of yam (varieties Florido (Δ) and Krenghè (\circ)) and potato (\blacksquare) starch gels (30 g dry starch/100 g gel). The lines correspond to trend lines.

of yam starches increased at a high rate and reached a plateau, whereas potato starch showed a less pronounced increase. E_D of aged starch gels (14 d) increased in the order potato < Krenghè < Florido. In contrast, σ_b of yam starches showed a smaller increase that leveled off after a few days, while potato starch showed a pronounced firming throughout the aging period.

The modulus of deformability (E_D) reflects the swelling state and the deformability of swollen granules, while the breaking stress gives information on the cohesion between the swollen granules [28, 29]. The present results suggest that the structural strength of yam starch granules is higher than that of potato starch. Firming of yam starch gels is very pronounced in the first days of aging, indicating that the reorganization of the amylose fraction plays an important role. This explains why no differences between the aged yam and potato starch gels were found with DSC (Tab. 3), because the melting of reorganized amylopectin is primarily measured. It should be added that the melting of ordered amylose cannot be readily followed by DSC, as it gives a phase transition in the high

temperature region. The results of the breaking stress suggest that the cohesion between yam starch granules is not as strong as between potato starch granules, due to restricted amylose leaching from yam starch. It is noteworthy that the modulus of deformability and the breaking stress of yam starch gels almost did not change during the second week of aging, which is rather atypical for a starch gel, but could be of interest for practical application.

4 Conclusions

Yam starch presents properties that are distinct from other tuber starches. Furthermore, the botanical manifoldness of the *Dioscorea* spp. results in yam starches with a rather broad range of properties. The physicochemical characterization methods such as X-ray diffraction, DSC and iodine titration reveal differences between the starches, but no straightforward relation between these properties and the thickening and gelling behavior as detected by rheological measurements could be established. On the other hand, the combination of hot-stage microscopy and rheology contributes to revealing the structure-property relationships of yam starch dispersions. The results suggest that the high structural strength of yam starch dispersions are due to a better preservation of the granular structure compared to tapioca and potato starches. A particularity of yam starch dispersions is that they show a high viscosity at low stress paired with a strong shear-thinning effect, which is generally desired in terms of texture. Based on the mechanical behavior of concentrated starch gels, it is hypothesized that swelling of yam starch is accompanied by a moderate release of amylose, but that this fraction dominates the gelling and short term aging behavior.

Isolated yam starch has a potential as thickening and gelling agent in food. On the other hand, detailed characterization of yam starch properties contributes to a better understanding of the textural properties of traditional yam products. An example is a pounded yam dish, called *foutou* in the Ivory Coast, where the texture is thought to be strongly related to the phase behavior of the starch fraction. Furthermore, non-food applications of yam starch as adhesive, package material or as biodegradable composite component are of interest [30]. In particular yam tubers of lower commercial value for direct consumption, for instance *D. alata*, could present a good source of yam starch. However, a better prediction of the performance of yam starch requires an improved understanding of the structural features of starch, that determine the colloidal properties of aqueous starch dispersions.

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