

## End Use Quality of Some African Corn Kernels. 2. Cooking Behavior of Whole Dry-Milled Maize Flours; Incidence of Storage

Christian Mestres,<sup>\*,†</sup> Mathurin Nago,<sup>‡</sup> Noël Akissoë,<sup>‡</sup> and Françoise Matencio<sup>†</sup>

CIRAD-CA, Laboratoire de Technologie des Céréales, Maison de la Technologie, 73 rue J.-F. Breton, B.P. 5035, 34032 Montpellier Cedex 1, France, and Faculté des Sciences Agronomiques, Département de Nutrition et Sciences Alimentaires, Université Nationale du Bénin, B.P. 526, Cotonou, Bénin

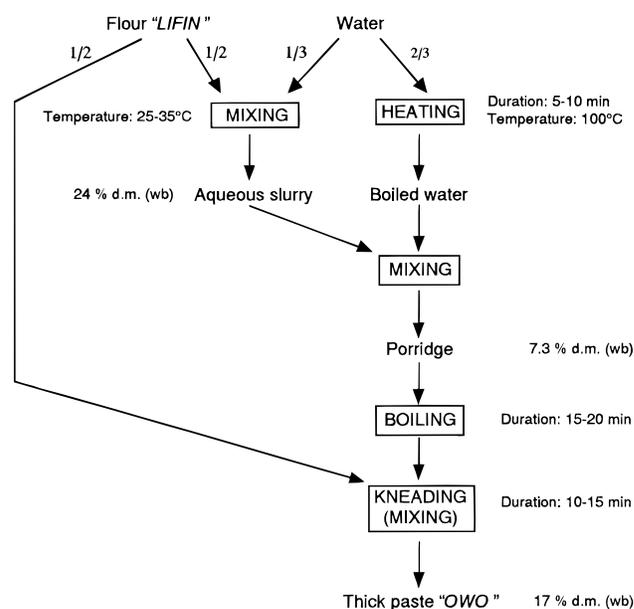
The pasting behavior of whole maize flours from 21 African maize cultivars (five local ecotypes and 16 new cultivars) was determined and compared to that of market flours from Cotonou (Benin). More viscous pastes were obtained from local ecotypes that were more friable and gave finer flours. Characteristics of solvent (concentration and composition) and dispersed (volume fraction, swelling power) phases of the pastes were determined: paste viscosity increased with the volume fraction of the dispersed phase and with its rigidity (evaluated by dry matter concentration of dispersed material), whereas solvent phase did not play any direct role on overall paste viscosity. Flour storage promoted the formation of fatty acids that could complex amylose during paste cooling; therefore, amylose solubility decreased after flour storage for several months, and paste viscosity at 50 °C increased due to some hardening of swollen particles.

**Keywords:** Maize; flour; storage; hot paste viscosity; swelling; solubility

### INTRODUCTION

In many African countries, maize is used for human consumption in various and numerous traditional forms (Nago, 1992), including two unfermented products that are generally the most common and popular (Nago et al., 1997): the porridge which is used as a weaning food and breakfast meal and the thick paste which is associated with sauces at lunch and dinner. The paste is markedly predominant in the daily human diet; in Benin particularly, a brief study revealed that more than 75% of the households consume regularly the maize thick paste named "owo" (Bertholon et al., 1975). In this country, more than 50% of the maize is used to prepare "owo" (Bertholon et al., 1975; Nago and Hounhouigan, 1990). It is prepared traditionally from a whole grain flour (the "lifin") through a complex and long established practice (Figure 1): nearly 5 L of water is necessary to cook 1 kg of "lifin". A very similar procedure is also used to prepare a thick paste from a sorghum flour in Mali for example (Fliedel, 1994). The dry matter concentration is close to 17% (wb) for the thick paste and near 8% (wb) for the porridge. A brief investigation (sample of 60 inhabitants) carried out in two regions of the south of Benin (one rural zone with high maize production, one urban area with high maize product consumption level) indicated that, concerning the thick paste, consumers look for high water absorption ability during cooking and high paste elasticity. Similarly in Togo, the main quality requirements are swelling ability during cooking and elasticity and consistency of the thick paste (Agossou et al., 1986). In the case of the sorghum thick paste of Mali, consumers look for high firmness (Fliedel, 1994).

Consumers are aware that maize grain quality may influence thick paste quality. Therefore they generally prefer local ecotypes (Koudokpon, 1991) with floury and



**Figure 1.** Flow sheet for the traditional preparation of the thick paste, owo, in Benin from whole dry-milled maize flour.

soft grains rather than new cultivars that have generally hard and vitreous kernels (Nago et al., 1996). However, no correlation was found by Fliedel (1994) between sorghum endosperm vitreousness or hardness and firmness of the thick paste. Moreover, very few publications relate maize grain quality to thick paste quality; the only ones dealing on fermented products (Adeyemi et al., 1987; Osungbaro, 1990). The present study was carried out to evaluate the ability of various cultivars from Benin (local ecotypes and new cultivars) to give good traditional end products (porridge and thick paste) and to determine which grain characteristic could correlate with end product quality; this could be used to better orient local maize breeding programs. Hot paste viscosities, measured using the Rapid Visco Analyzer, that correlate positively with firmness of

\* Author to whom correspondence should be addressed (fax +33 4 67 61 44 44; e-mail mestres@cirad.fr).

<sup>†</sup> CIRAD-CA.

<sup>‡</sup> Université Nationale du Bénin.

fermented porridge and thick paste (Okoli and Adeyemi, 1989) will be used to evaluate end product quality.

Moreover, consumers say that the age of grains and of whole grain flour affects the quality of resulting paste and porridge. Although some studies have been made on the impact of storage duration and storage conditions on biochemical and nutritional grain qualities (Onigbinde and Akinyele, 1988), no investigation was performed concerning the evolution of organoleptic and textural qualities of maize thick paste during grain and flour storage. This was the second objective of this study.

Besides, Fliedel (1994) observed the determinant role of starch characteristics in the texture of sorghum thick paste: firmness increased with starch amylose content and solubility at 85 °C but decreased with starch swelling power at this temperature. Indeed, starch pastes can be considered as suspensions of swollen particles dispersed in a macromolecular viscous matrix (Doublier et al., 1987a). It is therefore interesting to evaluate the contribution of solubilized and dispersed phases on the overall paste rheological behavior.

## EXPERIMENTAL PROCEDURES

**Materials.** We used six market traditional flours of Cotonou (Benin), among the eight already described in a previous paper (Nago et al., 1997). They were stored at 4 °C before analysis. Twenty-one samples of maize grains were collected in Benin; they originated from local ecotypes (five samples) and new cultivars (16 samples). Whole maize grains were ground successively through a KT-30 disc mill device (Falling Number) with fine burr at setting 1 and a Cyclotec 1093 sample mill (Tecator) using coarse (1 mm) aperture to produce laboratory-prepared whole maize flours. Whole maize flours were analyzed fresh just after processing or after storing in open air at 20 °C (in an air-conditioned room) or 35 °C (in an oven) for 15 days to 4 months.

**Fat Acidity.** Fat acidity was determined in duplicate after extraction with toluene [AACC, 1983 (Method 02–03A)].

**Hot Paste Viscosity.** Hot starch dispersion viscosity profiles were obtained using a Rapid Visco Analyzer model 3D (Newport Scientific, Narrabeen, Australia). Flour (2, 3, or 3.5 g of dry matter) was first dispersed in spring water (Evian, France) for a total amount of 28 g using an Ultraturax T25 (Ika, Staufen, Germany). Dry matter concentrations within the dispersions were 7.1, 10.7, and 12.5% (wb) respectively, that is, in the range of porridge dry matter concentration (nearly 8%, wb). However, it was impossible to use higher concentrations, closer to that of the thick paste. Viscosity was recorded using the following temperature profile: holding at 35 °C for 3 min, heating to 95 °C at 6 °C min<sup>-1</sup>, holding at 95 °C for 5 min, and then cooling to 50 °C at 6 °C min<sup>-1</sup>. Three parameters were measured: viscosity at the beginning of the plateau at 95 °C (13 min,  $V_{95b}$ ), viscosity at the end of the plateau at 95 °C (18 min,  $V_{95e}$ ), and final viscosity (25 min 30 s,  $V_{fin}$ ).

**Swelling and Solubility Measurements.** Swelling power and solubility of pasted flours were determined on 8% (wb) flour dispersions (i.e., 2.25 g of dry matter (dm) dispersed in 28 g). The RVA was used to prepare the pastes as described above, but the experiment was either stopped after 13 min (at the beginning of the plateau at 95 °C) or after 18 min (at the end of the plateau at 95 °C) or let go to its end. The paste was immediately transferred to a 50 mL centrifuge tube. After centrifugation for 5 min at 5000g and 25 °C the supernatant and sediment were collected and weighed ( $W_{SU}$  and  $W_{SE}$ , respectively). They were then dried at 100 °C for 24 and 48 h, respectively, and their dry matter mass determined ( $D_{SU}$  and  $D_{SE}$ , respectively). Four parameters were calculated: first, the solubility index ( $S$ ) and the swelling power ( $G$ ) that were defined (formulas 1 and 2) according to Leach et al. (1959), and second, the concentration of solubilized material ( $SM$ ) in the supernatant and the volume fraction of the dispersed phase ( $\phi$ , formulas 3 and 4):

$$S (\% \text{ db}) = 100 \times D_{SU}/2.25 \quad (1)$$

$$G (\text{g/g}) = (W_{SE} - D_{SE})/D_{SE} \quad (2)$$

$$SM (\text{mg/mL}) = D_{SU}/(W_{SU} - D_{SU}) \quad (3)$$

$$\phi = (27.25 - (W_{SU} - D_{SU}))/27.25 \quad (4)$$

where 27.25 is the calculated total volume (cm<sup>3</sup>) of the paste considering that the specific density of the flour is 1.5 g/cm<sup>3</sup>.

We also measured starch and amylose content of the supernatant using a procedure derived from that of Magel (1991). An aliquot of the supernatant (100 or 200  $\mu$ L) was placed in a 100 mL flask. Ultrapure water and then 1 mL of 1.0 N acetic acid and 2 mL of I<sub>2</sub>/KI solution (0.2 and 2% w/v, respectively) were added. After shaking, the volume was adjusted to 100 mL with ultrapure water and the flask was placed in darkness. The absorbance of the samples at 620 and 545 nm ( $S_{620}$  and  $S_{545}$ ) were read after 20 and 25 min, respectively. Two standard curves for amylose and amylopectin were performed each day. For this, stock solutions of amylose and amylopectin were prepared according to the hot procedure of ISO # 6647 (1987). On one hand, four aliquots (0.5, 1.0, 1.5, and 3.0 mL) of the amylose stock solution and, on the other hand, three aliquots (2.5, 5.0, and 10 mL) of the amylopectin stock solution were used, and their absorbances were measured as previously described. Linear regression coefficients were calculated for the absorbances of amylose ( $Y_{620}$  and  $Y_{545}$ ) and amylopectin ( $P_{620}$  and  $P_{545}$ ) at 620 and 545 nm, respectively: correlation coefficients were always over 0.995. Starch and amylose contents within dosimetric flasks were calculated according to the formulas 5–7:

$$\text{amylose (Amy, } \mu\text{g/mL)} = \frac{P_{620}S_{545} - P_{545}S_{620}}{P_{620}(Y_{545} - P_{545}) - P_{545}(Y_{620} - P_{620})} \quad (5)$$

$$\text{starch (Sth, } \mu\text{g/mL)} = \frac{S_{620} - \text{Amy}(Y_{620} - P_{620})}{P_{620}} \quad (6)$$

$$\text{amylose (\% starch basis)} = \frac{\text{Amy} \times 100}{\text{Sth}} \quad (7)$$

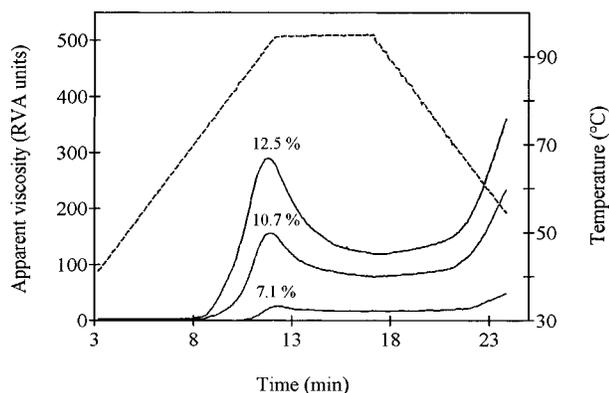
The accuracy of the procedure was fairly good for solutions having starch content ranging from 13.5 to 27  $\mu$ g/mL and amylose content ranging from 25 to 75% (starch basis). Starch and amylose concentrations were multiplied by 500 or 1000 to calculate actual concentrations in supernatant.

**Differential Scanning Calorimetry.** Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC 7 device (Perkin Elmer, Norwalk, CT) using hermetic inox pans. The sample pan (10–11 mg of sample and 50  $\mu$ L of ultrapure water) and the reference pan (60  $\mu$ L of ultrapure water) were heated from 30 to 95 °C at a scanning rate of 6 °C min<sup>-1</sup>, held at 95 °C for 5 min, and then cooled to 30 °C at 6 °C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

**Analysis of Market Flours.** The rheological behavior of six whole maize market flours (lifen) was first determined in order to obtain reference data on traditional products. The shape of hot paste viscosity curves obtained with the RVA was similar for all samples (see for example Figure 2) with a first maximum viscosity at (or close to) 95 °C, a thinning phenomenon during the plateau at 95 °C and an increase of viscosity during cooling. This last phenomenon presented two steps: a gentle slope from 95 to 70–65 °C followed by a steep slope till 50 °C. Final viscosity was always over peak viscosity close to 95 °C.

An analysis of variance showed a significant sample effect for  $V_{95b}$  and  $V_{fin}$  (Table 1). Finer flours gave more viscous pastes: the correlation coefficient between the



**Figure 2.** Temperature (dotted line) and apparent viscosity (plain lines) profiles obtained during pasting a maize market flour (with 7.1, 10.7, and 12.5% dry matter content, wb) of Cotonou (Benin).

**Table 1. Apparent Viscosities of Pastes Made with Market Flours (Mean Values for 7.1, 10.7 and 12.5% dm Suspensions)**

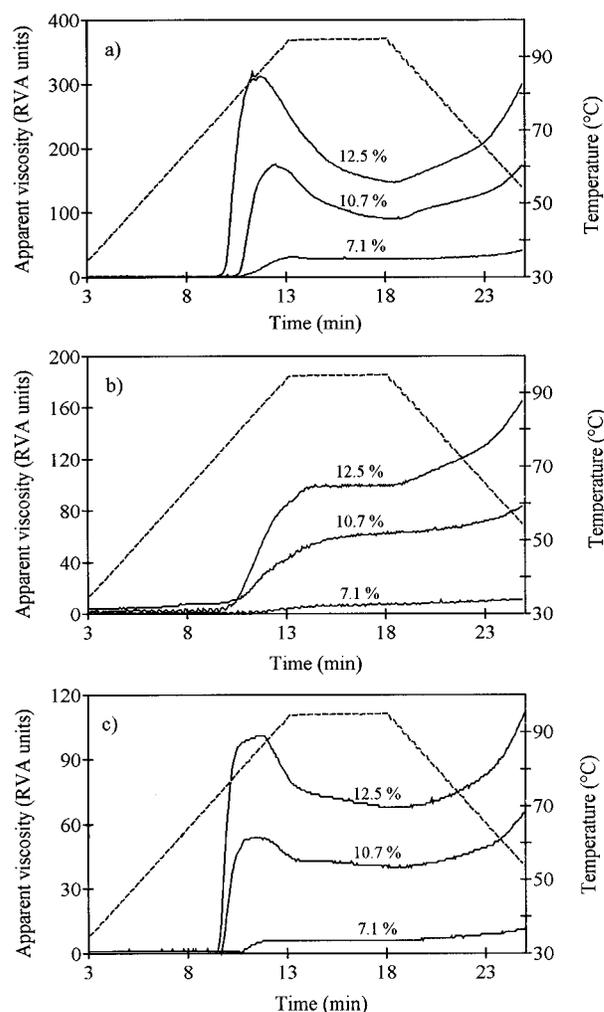
	beginning (95 °C) <sup>a</sup>	end (95 °C) <sup>b</sup>	final (50 °C) <sup>c</sup>
mean	134	70	249
range	95–168	61–81	197–294
LSD <sup>d</sup>	42	14	58

<sup>a</sup> After heating from 35 to 95 °C at 6 °C/min. <sup>b</sup> After heating from 35 to 95 °C at 6 °C/min and holding at 95 °C for 5 min. <sup>c</sup> After heating from 35 to 95 °C at 6 °C/min, holding at 95 °C for 5 min, and then cooling at 50 °C at 6 °C/min. <sup>d</sup> Least significant difference at 0.05 level for the sample effect.

percentage of flours passing through a 315  $\mu\text{m}$  sieve (previously measured; Nago et al., 1997) and  $V_{95b}$  was highly significant (0.85). Other physicochemical characteristics of market flours were not correlated with hot paste viscosities.

**Rheological Behavior of Freshly Laboratory Prepared Whole Maize Flours.** Various viscosity profiles were obtained: some presented a viscosity peak before 95 °C (Figure 3a) whereas others had no viscosity peak (Figure 3b). Higher viscosities at 95 °C were observed for profiles having a viscosity peak. The paste from TZB-SE-SR flour was an exception: it presented a peak viscosity close to 90 °C but had a very low viscosity at 95 °C (Figure 3c, Table 2). Viscosity profiles were similar for each flour sample at the two highest dry matter concentrations. An analysis of variance indicated, apart from a significant dry matter effect (not shown), a significant cultivar effect for the three viscosities (Table 2). Local ecotypes generally gave the thickest hot pastes. Newman–Keuls multiple mean comparisons showed that Gbaévé, Gbogboué, Gnonli, and Djakpé belonged in the same homogeneous class for  $V_{95e}$  and  $V_{fin}$ . Their  $V_{95e}$  mean value (80 RVA units) was close to that observed for the six market flours (70 RVA units, Table 1). Gnonli paste was significantly more viscous than all other pastes at the beginning of the profile; and it had a  $V_{95b}$  (147 RVA units) close to that observed for market flours (134 RVA units). But after cooling at 50 °C, the pastes made with local ecotypes and new cultivars had apparent viscosities at least half as high as that measured for market flours (Table 1).

The three viscosity variables were placed on the correlation circle obtained by the principal component analysis (Figure 4) of the physicochemical characteristics of grains and flours (Nago et al., 1997); they were located in the first quarter of the plan formed by the two first axes.  $V_{95b}$  was particularly correlated with the first axis, which represented grain mechanical at-



**Figure 3.** Temperature (dotted line) and apparent viscosity (plain lines) profiles obtained during pasting (at 7.1, 10.7, and 12.5% dry matter content, wb) fresh laboratory-prepared whole maize flours from Gnonli (a), Sékou 85 (b), and TZB-SE-SR (c).

tributes and flour physical characteristics; the highest correlation coefficients were between  $V_{95b}$  and friability or flour fineness (percentage of passing through 150  $\mu\text{m}$  sieve; 0.88 and 0.75, respectively). Sefah-Dedeh (1989) also found that finer flours gave more viscous hot pastes, whereas Fliedel and Yajid (1992) showed that finer sorghum flours gave firmer thick pastes. A multiple regression analysis showed that friability index (Fri) and flour free lipid content (Lip) could explain 86% of the variability of  $V_{95b}$ :

$$V_{95b} = -24.7 + 3.34\text{Fri} - 14.4\text{Lip} \quad (8)$$

$V_{95e}$  and  $V_{fin}$  were located in an intermediate position between the two first axes, and only 59% of  $V_{fin}$  variability was explained from Fri and flour starch content (Sth):

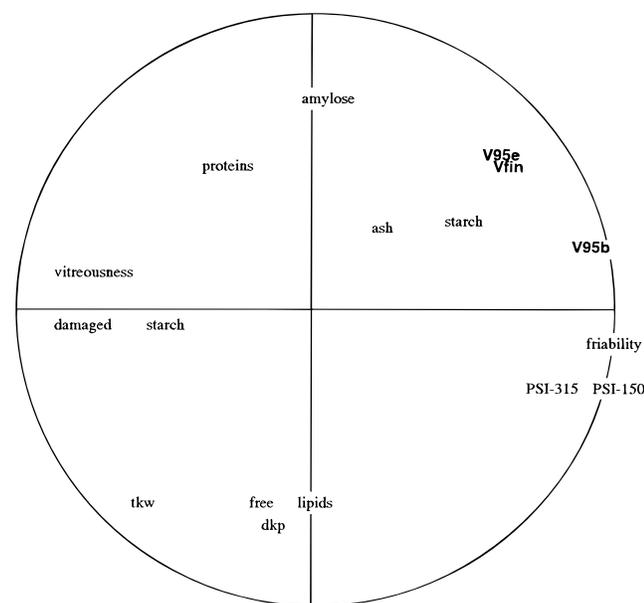
$$V_{fin} = -5.42 + 1.53\text{Fri} + 8.0\text{Sth} \quad (9)$$

Thus grain friability, and consequently fineness of obtained flour, is the first factor involved in hot paste rheological properties; the more friable the grain, the finer the flour and the more viscous the paste. This explains that local ecotypes that had higher friability indexes gave more viscous hot pastes, close to those obtained for market flours.

**Table 2. Apparent Viscosities of Pastes Made with Fresh Laboratory-Prepared Whole Maize Flours from 21 Cultivars**

cultivars	apparent viscosity (RVA units) <sup>a</sup>		
	beginning (95 °C) <sup>b</sup>	end (95 °C) <sup>c</sup>	final (50 °C) <sup>d</sup>
local ecotypes			
Gbaévé	76	78	141
Gbogboué	84	79	134
Gnonli	147	90	172
Gougba	63	65	119
Djakpé	75	74	150
new cultivars			
DMR-ESR-W	47	59	101
Poza Rica 7843-SR	35	53	77
Pirsabak7930 SR	42	57	97
Sékou 85	42	54	84
B. M. L.	51	61	110
DMR-ESR-W x 28 Synthetic 1	46	63	116
Gbogboué × TZSR-W	50	59	107
AB 11	50	56	104
AB 12	54	58	102
AB 13	41	54	102
NH2-SR	42	62	109
TZSR-W	33	49	86
TZB-SE-SR	44	38	64
TZPB-SR	33	52	91
Sékou 85 × TZSR-W	30	46	83
La Posta	32	52	88
mean	53	60	107
LSD <sup>e</sup>	33	14	34

<sup>a</sup> Mean value for the three dry matter concentrations: 7.1, 10.7, and 12.5% (wb). <sup>b</sup> After heating from 35 to 95 °C at 6 °C/min. <sup>c</sup> After heating from 35 to 95 °C at 6 °C/min and holding at 95 °C for 5 min. <sup>d</sup> After heating from 35 to 95 °C at 6 °C/min, holding at 95 °C for 5 min, and then cooling to 50 °C at 6 °C/min. <sup>e</sup> Least significant difference at 0.05 level for the cultivar effect.



**Figure 4.** Plotting RVA apparent viscosities (at the beginning of the plateau at 95 °C,  $V_{95b}$ , at the end of the plateau at 95 °C,  $V_{95e}$ , and at 50 °C,  $V_{fin}$ ) of fresh laboratory-prepared whole maize flours on the correlation circle of the 12 normalized variables of the physicochemical attributes of maize kernels (Nago et al., 1997). First and second components as first and second axes, respectively. Tkw is thousand kernel weight, dkp is dent kernel percentage, and PSI-150 and PSI-315 are particle size indices measured with 150 and 315  $\mu$ m sieves, respectively.

**Storage Behavior of Laboratory-Prepared Whole Maize Flours.** Laboratory-prepared whole maize flours from three cultivars (two local ecotypes, Gnonli and

**Table 3. Evolution with Temperature and Storage Duration of Fat Acidity (mg of KOH/100 g of dm) of Laboratory-Prepared Whole Maize Flours from Three Cultivars**

cultivar	storage temp (°C)	storage duration				
		15 days	1 month	2 months	3 months	4 months
Gnonli	20	95	135	185	200	230
	35	95	140	180	225	235
Gougba	20		140	180	225	270
	35		140	180	195	225
Pirsabak	20		100	130	180	195
7930 SR	35		100	125	150	160
mean values			125	160	200	220
LSD <sup>a</sup> for the storage duration effect						13
LSD <sup>a</sup> for the cultivar effect						11
LSD <sup>a</sup> for the storage temperature effect						9
standard deviation of the residual (df = 6)						9

<sup>a</sup> Least significant difference at 0.05 level.

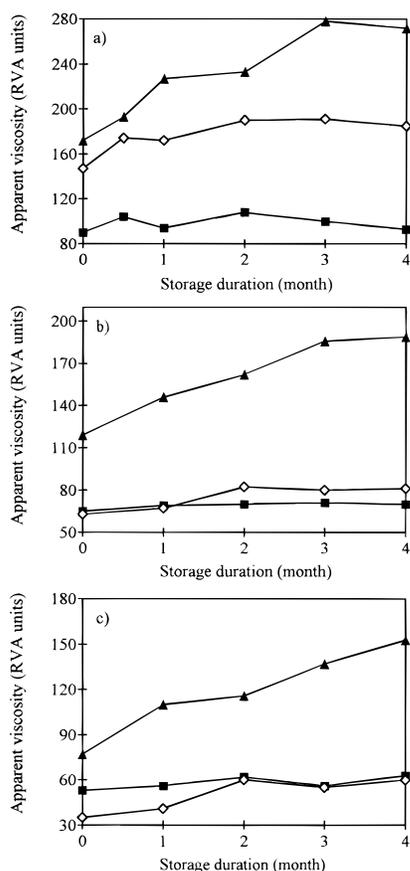
Gougba, and one new cultivar, Pirsabak 7930 SR) were stored in open air for 15 days to 4 months at 20 or 35 °C (Table 3). Flour water content remained close to 13% after storage at 20 °C, whereas a significant drying procedure occurred at 35 °C: flour water content was close to 8% (wb) after 4 months at this temperature. Fat acidity increased during storage (it was between 31 and 48 mg of KOH/100 g of dm for fresh flours; Nago et al., 1997) and particularly during the first 3 months (Table 3), but it was never as high as for market flours (fat acidity over 300, Nago et al., 1997). Fat acidity was significantly higher for flours stored at 20 °C. Flour from Pirsabak 7930 SR had lower fat acidity than the two others in spite of its higher free lipid content (Nago et al., 1997). Indeed, Pirsabak 7930 SR flour was coarser (Nago et al., 1997), and a less intimate mixing of lipid substrate and lipolytic enzyme could explain that lipolysis was slowed down. An other explanation should be that Pirsabak 7930 SR was poorer in lipolytic enzymes.

Hot paste viscosities were measured for all samples at the three dry matter concentrations (7.1, 10.7, and 12.5% wb) and an analysis of variance was performed considering the dry matter concentration factor as a controlled term. Apart from highly significant drier matter concentration and cultivar effects (the latter confirming previous results obtained on the 21 samples), no significant storage temperature effect could be evidenced. However, the three viscosities increased significantly with storage duration (Figure 5): this phenomenon was particularly important for the final viscosity of the flour stored 4 months, which was close to that of market flour.

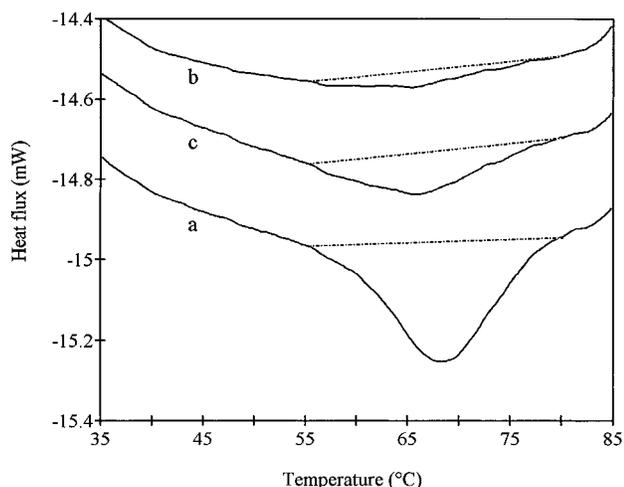
**Swelling and Solubility Patterns.** Hot starch pastes can be considered as suspensions of swollen particles dispersed in a macromolecular viscous matrix (Doublie et al., 1987a). Both phases contribute to overall rheological properties of the paste. It is therefore necessary to evaluate the relative contribution of each phase in order to understand the rheological behavior of a paste.

Swelling and solubility patterns were studied for pastes made with four market flours and with nine laboratory-prepared whole maize flours (four from local ecotypes and five from new cultivars, Table 4). It can be noticed first that dry matter and starch concentrations measured in solvent phase were always in very close agreement. This validates the methodology of determination of starch and amylose concentrations.

Swelling and solubility patterns were found very similar for the various pastes made with the four



**Figure 5.** Evolution with storage duration of RVA apparent viscosities (at the beginning of the plateau at 95 °C, ■; at the end of the plateau at 95 °C, ◇; and after cooling to 50 °C, ▲) of pastes made with laboratory-prepared whole maize flours from Gnonli (a), Gougba (b), and Pirsabak 7930 SR (c); mean values of 20 and 35 °C storage conditions.



**Figure 6.** Cooling curves obtained by differential scanning calorimetry (for details see the text) for market flour (a) and laboratory-prepared whole maize flours from Gnonli, fresh (b) or after storage at 20 °C for 4 months (c).

market flours; only mean values are thus reported (Table 4). Starch swelling and solubilization increased during the plateau at 95 °C but remained rather low: 3–10 times lower than for maize starch pastes prepared in similar conditions (Dublier et al., 1987b). This difference may be due to the larger particle size of market flours (almost 10 times weight average diameter of maize starch, 15  $\mu\text{m}$ ; Swinkels, 1985) that hindered macromolecule leaching and particle swelling. During cooling to 50 °C, the swelling power ( $G$ ) and volume

fraction of the dispersed phase ( $\phi$ ) remained constant or decreased slightly whereas starch solubility decreased dramatically. In particular, the amylose fraction that represented nearly 40% of the solubilized starchy material at 95 °C, accounted for less than 10% at 50 °C. In parallel, with the the same temperature profile as for RVA experiments, an exotherm at a peak temperature close to 70 °C was observed by differential scanning calorimetry during the cooling step (Figure 6a). This can be interpreted as the enthalpy of formation of complexes between amylose and monoacyl lipids (Bulpin et al., 1982; Eliasson and Krog, 1985; Biliaderis et al., 1985). Indeed market flours are rich in free fatty acids (Nago et al., 1997) that are able to complex amylose. It has to be noted that complex formation appeared at the same temperature as the change (increase) in the slope of apparent viscosity (Figure 2). Hence it can be concluded that, during the cooling step, complexes between amylose and free fatty acids are made, thus decreasing amylose solubility and increasing apparent viscosity of the paste (Table 4).

Swelling and solubility patterns of various local ecotypes were very similar except that volume fraction and swelling power of the dispersed phase were significantly higher for Gnonli (Table 4). This may be linked to the extreme fineness of this flour (median particle size less than 125  $\mu\text{m}$ ; Nago et al., 1997) that facilitates particle swelling. New cultivars presented similar characteristics of the dispersed phase ( $\phi$  and  $G$ ) as local ecotypes (except Gnonli) but presented higher dry matter and starch concentrations after cooling. The amylose content of the solubilized fraction after paste cooling to 50 °C was higher for fresh laboratory-prepared flours (40–50% starch basis, sb) than for market flours (less than 10% sb, Table 4). Indeed, fat acidity of fresh laboratory-prepared whole maize flours was lower (Nago et al., 1997) and only few amylose–monoacyl lipid complexes could be detected by differential scanning calorimetry (Figure 6b).

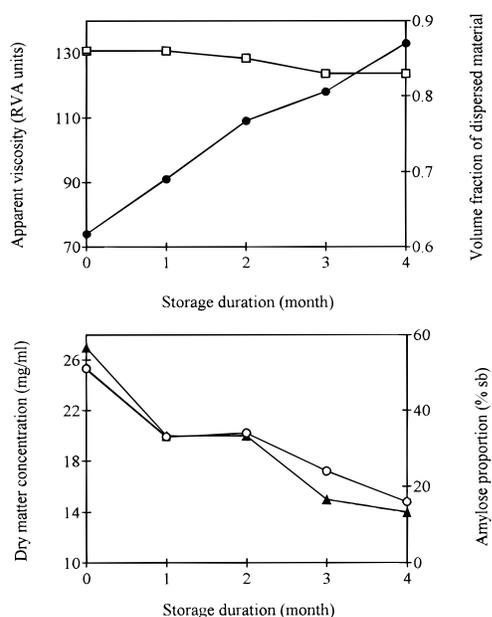
Swelling and solubility determinations were also performed for stored Gnonli flours (1–4 months at 20 °C). The characteristics of the paste dispersed phase did not vary significantly with flour storage; for example at 50 °C,  $\phi$  was 0.86 for the fresh flour and 0.83 after storage for 4 months (Figure 7). On the other hand, the characteristics of paste solvent phase dramatically changed due to flour storage. In particular for cooled pastes, dry matter and starch concentrations were half as high after 4 months storage than before (Figure 7). Furthermore, amylose accounted for 16% of solubilized starch for a paste made with stored flour compared 51% for a fresh flour. Differential scanning calorimetry revealed (Figure 6c) that this drop in amylose solubility was, as for market flours, linked to amylose complexation with free fatty acids, whose concentration increased during storage (Table 3).

Taking measurements all together (either from market flours or from laboratory prepared whole maize flours), apparent viscosities measured at 95 °C increased with  $\phi$ , following a pseudoexponential law (Figure 8). A replot of  $AV/\phi$  versus  $\phi$  according to Bagley and Christianson (1982) did not give a better master curve. The deformability (or inversely, the rigidity) of the particles also influences overall viscosity of a suspension; this effect becomes more and more important when  $\phi$  increases (Dublier et al., 1987b; Steeneken, 1989). In the case of a starch paste, particle rigidity can be evaluated by starch concentration within dispersed particles which can be estimated by the ratio  $1/G$  (Dublier et al., 1987b; Steeneken, 1989). But, this

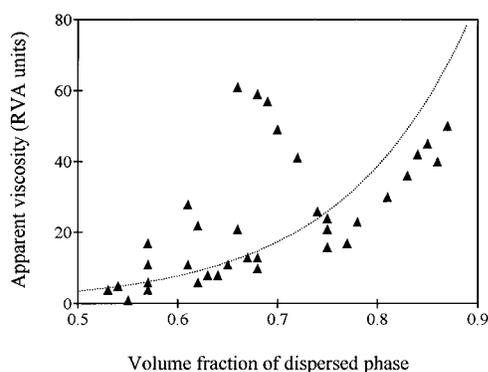
**Table 4. Characterization of Solubilized and Dispersed Material and Viscosities of 8.0% Pastes Prepared with Market Flours of Cotonou (Benin) and Fresh Laboratory-Prepared Whole Maize Flours**

sample	stage	$S^d$ (% db)	solubilized material			dispersed material		apparent viscosity (RVA units)
			dry matter concentration (mg/mL)	starch concentration (mg/mL)	amylose (% starch basis)	$\phi^e$	$C^f$ (g/g)	
market flours <sup>a</sup>	95b <sup>g</sup>	6.3	12	12	30	0.59	6.5	20
	95e <sup>h</sup>	8.8	32	32	41	0.77	9.3	25
	final <sup>i</sup>	5.5	19	18	6	0.76	8.5	95
Gnonli	95b <sup>g</sup>	8.0	26	27	58	0.72	8.7	41
	95e <sup>h</sup>	7.5	35	34	55	0.83	10.1	36
	final <sup>i</sup>	4.9	28	27	51	0.86	10.0	67
local ecotypes <sup>b</sup>	95b <sup>g</sup>	11.4	22	23	55	0.58	6.8	6
	95e <sup>h</sup>	13.0	34	35	58	0.69	8.5	16
	final <sup>i</sup>	9.4	29	29	47	0.74	8.7	31
new cultivars <sup>c</sup>	95b <sup>g</sup>	13.1	27	27	48	0.59	7.1	7
	95e <sup>h</sup>	14.2	36	35	50	0.68	8.4	13
	final <sup>i</sup>	10.5	33	33	41	0.74	8.6	23

<sup>a</sup> Mean values for four market flours. <sup>b</sup> Mean values for Gbaévé, Gbogboué, and Gougba samples. <sup>c</sup> Mean values for Poza Rica 7843-SR, Pirsabak 7930-SR, AB 12, TZB-SE-SR, and TZPB-SR samples. <sup>d</sup> Solubility index. <sup>e</sup> Volume fraction of the dispersed phase. <sup>f</sup> Swelling power. <sup>g</sup> After heating from 35 to 95 °C at 6 °C/min. <sup>h</sup> After heating from 35 to 95 °C at 6 °C/min and holding at 95 °C for 5 min. <sup>i</sup> After heating from 35 to 95 °C at 6 °C/min, holding at 95 °C for 5 min, and then cooling at 50 °C at 6 °C/min.



**Figure 7.** Evolution with flour storage duration at 20 °C of the characteristics of the pastes (at 50 °C) made with laboratory prepared Gnonli flours: RVA apparent viscosity, ●; volume fraction of dispersed material, □; dry matter concentration, ▲; and amylose proportion, ○, in solvent phase.



**Figure 8.** Relationship between apparent hot paste viscosities measured at 95 °C and volume fraction of dispersed phase.

hypothesizes that there is no solubilized macromolecule within the swollen starch granule. With this hypothesis, the solubility index ( $S$ ) of Gnonli flour was lower after 5 min at 95 °C than at the beginning of the plateau at 95 °C (Table 4). Since it is difficult to imagine that

starch solubility decreased during the plateau at 95 °C, it can be inferred that part of solubilized starch was present in the solvent within swollen starch granules. Furthermore, we can assume that a diffusion equilibrium was achieved in the paste and that the concentration in solubilized polysaccharides was similar in and out of the swollen starch granules. In this case, the concentration of the dispersed material ( $C_{DM}$ ) can be calculated with the formula (10):

$$C_{DM} \text{ (mg/mL)} = 1000/G - SM \quad (10)$$

where  $G$  is the swelling power (g/g) and  $SM$  the concentration of solubilized material (mg/mL) in the solvent phase.

We could thus fit our results of apparent viscosity at 95 °C with  $\phi$  and  $C_{DM}$  (Figure 9) according to the following empirical power law (11):

$$AV \text{ (RVA units)} = 2.1 \times 10^{-4}(\phi - 0.5)^{2.3} C_{DM}^{3.4} \quad (11)$$

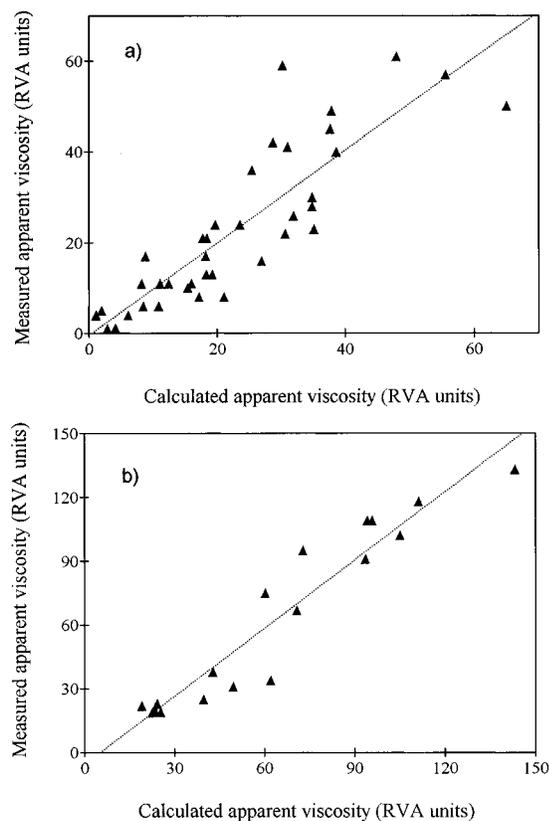
It explained 76% ( $r^2$ ) of the variability of apparent viscosity. We could also fit apparent viscosities at 50 °C with a very similar power law (12):

$$AV \text{ (RVA units)} = 4.4 \times 10^{-4}(\phi - 0.5)^{2.9} C_{DM}^{3.5} \quad (12)$$

It explained 91% ( $r^2$ ) of the variability of apparent viscosities at 50 °C (Figure 9).

It has to be noted that the apparent viscosity decreased when dry matter concentration in the solvent phase increased; this meant that the viscosity of the solvent phase had no measurable direct contribution to overall viscosity of the paste, otherwise the opposite relationship should be observed.

Starch damage did not seem to have a great influence on solubility/swelling behavior of starch and on hot paste rheological properties. Indeed, swelling and solubility of flours from new cultivars, that had higher damage starch, were not clearly higher than for local ecotypes. It is likely that the granule size effect was more important and could hide the starch damage effect (these two parameters were negatively correlated; Nago et al., 1997); Gnonli, that gave a very fine flour with very low starch damage had the higher swelling power and solubility (at least in the first part of the pasting process). Besides, market flours that had very high damaged starch percentages had very low starch solu-



**Figure 9.** Relationship between calculated (using  $\phi$  and SM) and measured (using RVA) apparent hot paste viscosities at 95 °C (a) and 50 °C (b).

bility. This was likely due to the amylose complexation effect that hid the potential damaged starch effect.

## CONCLUSION

Local ecotype maizes gave more viscous pastes than new cultivars. In particular, the paste made with Gnonli flour was the most viscous and was very similar to the pastes made with market flours. Consumers who want viscous porridges and elastic pastes should thus prefer porridges and pastes from local ecotypes. However, organoleptic tests will be performed in the near future in order to confirm this result.

Viscosity of the solvent phase did not play a significant role on the viscosity of the paste. However, the characteristics of the dispersed phase (its volume fraction and rigidity, estimated by dry matter concentration of dispersed material) explained more than 75% of the variability of overall paste viscosity.

Paste viscosity increased with flour fineness (or grain friability) due to the higher swelling capacity of fine flour particles. Flour storage promoted the formation of fatty acids that could complex amylose during paste cooling; therefore, amylose solubility decreased after several months of storage, and paste viscosity at 50 °C increased due to some hardening of swollen particules.

## LITERATURE CITED

- AACC. *Approved Methods of the AACC*; American Association of Cereal Chemists: St. Paul, MN, 1983.
- Adeyemi, I. A.; Osunsami, A. T.; Fakorede, M. A. B. Effect of corn varieties on ogi quality. *J. Food Sci.* **1987**, *52*, 322–325.
- Agossou, Y.; Afoda, D.; Lare, L.; Sewonou, K.; Tagba, B. *Tests de technologie traditionnelle de transformation des vivriers.*

*Synthese des travaux 1982–1985*; Société Togolaise du Coton: Lomé, Togo, 1986.

- Bagley, E. B.; Christianson, D. D. Swelling capacity of starch and its relationship to suspension viscosity—effect of cooking time, temperature and concentration. *J. Texture Stud.* **1982**, *13*, 115–126.
- Bertholon; Berger; Bastardis. *Etude de factibilité technico-économique d'un projet de maïserie au Bénin*; SATEC: Paris, France, 1975.
- Biliaderis, C. G.; Page, C. M.; Slade, L.; Sirett, R. R. Thermal behavior of amylose–lipid complexes. *Carbohydr. Polym.* **1985**, *5*, 367–389.
- Bulpin, P. V.; Welsh, E. J.; Morris, E. R. Physical characterization of amylose fatty-acid complexes in starch granules and in solution. *Starch* **1982**, *34*, 335–339.
- Doublier, J.-L.; Paton, D.; Llamas, G. A rheological investigation of oat starch pastes. *Cereal Chem.* **1987a**, *64*, 21–26.
- Doublier, J.-L.; Llamas, G.; Le Meur, M. A rheological investigation of cereal starch pastes and gels. Effect of pasting procedures. *Carbohydr. Polym.* **1987b**, *7*, 251–275.
- Eliasson, A.-C.; Krog, N. Physical properties of amylose–monoglyceride complexes. *J. Cereal Sci.* **1985**, *3*, 239–248.
- Fliedel, G. Evaluation de la qualité du sorgho pour la fabrication du tô. *Agric. Dev.* **1994**, *4*, 12–21.
- Fliedel, G.; Yajid, M. Effect of milling on sorghum tô quality. Presented at the 9th International Cereal and Bread Congress, Paris, France, 1–5 June 1992.
- ISO Method # 6647. *Rice—Determination of amylose content*; ISO: 1987.
- Koudokpon, V. Pourquoi les variétés améliorées de maïs ne sont-elles pas largement adoptées par les paysans? *Bull. Rech. Agron. Bénin* **1991**, *2*, 6–9.
- Leach, H. W.; McCowen, L. D.; Schoch, T. J. Structure of the starch granule. I. Swelling and solubility patterns of various starches. *Cereal Chem.* **1959**, *36*, 534–544.
- Magel, E. Qualitative and quantitative determination of starch by a colorimetric method. *Starch* **1991**, *43*, 384–387.
- Nago, M. C. *Street foods in West Africa*; FAO: Rome, Italy, 1992.
- Nago, M.; Akissoë, N.; Matencio, F.; Mestres, C. End use quality of some African corn kernels. 1. Physicochemical characteristics of kernels and their relationship with the quality of lifin, a traditional whole dry-milled maize flour from Benin. *J. Agric. Food Chem.* **1997**, *45*, 555–564.
- Nago, M. C.; Hounhouigan, J. *La technologie traditionnelle du maïs en pâte fermentée*; UNB/FSA: Abomey Calavi, Bénin, 1990.
- Okoli, E. C.; Adeyemi, I. A. Manufacturing of Ogi from malted (germinated) corn (*Zea Mays*): Evaluation of chemical, pasting and sensory properties. *J. Food Sci.* **1989**, *54*, 971–973.
- Onigbinde, A. O.; Akinyele, I. O. Biochemical and nutritional changes in corn (*Zea mays*) during storage at three temperatures. *J. Food Sci.* **1988**, *53*, 117–119, 123.
- Osungbaro, O. T. Effect of differences in variety and dry milling of maize on textural characteristics of ogi (fermented maize porridge) and agidi (fermented maize meal). *J. Sci. Food Agric.* **1990**, *52*, 1–11.
- Sefa-Dedeh, S. Effects of particle size on some physicochemical characteristics of “agbelima” (cassava dough) and corn dough. *Trop. Sci.* **1989**, *29*, 21–32.
- Steeneken, P. A. M. Rheological properties of aqueous suspensions of swollen granules. *Carbohydr. Polym.* **1989**, *11*, 23–42.
- Swinkels, J. J. Composition and properties of commercial native starches. *Starch* **1985**, *37*, 1–5.

Received for review July 31, 1996. Revised manuscript received November 15, 1996. Accepted November 25, 1996.\*

JF9605660

\* Abstract published in *Advance ACS Abstracts*, February 1, 1997.