

# Fractionation and Reconstitution Experiments Provide Insight into the Role of Gluten and Starch Interactions in Pasta Quality

J. A. Delcour,<sup>\*,†</sup> J. Vansteelandt,<sup>†</sup> M.-C. Hythier,<sup>‡</sup> J. Abécassis,<sup>‡,§</sup> M. Sindic,<sup>||</sup> and C. Deroanne<sup>||</sup>

Laboratory of Food Chemistry, Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, B-3001 Heverlee, Belgium, Unité de Technologie des Céréales et des Agropolymères, INRA, 2 Place Viala, F-34060 Montpellier, France, and Department of Agro-Industries, Agricultural State University, Passage des Départés, B-5030 Gembloux, Belgium

Commercial durum wheat (*Triticum durum* desf.) semolina was fractionated into starch, gluten, and water extractables. Starch surface proteins and surface lipids were removed, and two starches with manipulated granule size distributions were produced to influence starch properties, affecting its interaction with other semolina components. Reconstituted spaghetti was made with untreated (control) or treated starches. The pasta made from the starting semolina material had lower cooking time and was of lower quality than the samples made from reconstituted material. This was not due to changes in gluten properties as a result of the first step of the fractionation process. For the reconstituted samples, starch interaction behavior was not changed after surface protein or surface lipid removal. Starch surface properties thus do not influence the starch interaction behavior, indicating that starch–gluten interaction in raw (uncooked) pasta is mainly due to physical inclusion. All reconstituted pasta samples also had generally the same cooking quality. It was concluded that the small changes in starch gelatinization behavior, caused by the above-mentioned starch modifications, are of little importance for pasta quality.

**Keywords:** *Reconstitution; gluten; starch interactions; pasta quality*

## INTRODUCTION

Although in the past durum wheat (*Triticum durum* desf.) semolina proteins have been recognized as of utmost importance for pasta quality, it is at present accepted that more insight into the role of starch is necessary for further quality improvement. Indeed, the starch in pasta is no longer considered to be an inert filler. It can be a substantial, active, and thus quality-determining part of the pasta structure, and this may, among other phenomena, be because of its interactions with other semolina components (Preston, 1998).

Earlier studies, including reconstitution studies, have already attempted to elucidate the role of starch in pasta quality.

Sheu et al. (1967) were the first to apply fractionation and reconstitution techniques to pasta production. Durum semolina and hard red spring wheat farina were fractionated into their components (starch, gluten, sludge, and water extractables), and reconstituted mixtures were formed by systematic interchange of the various fractions. The reconstituted raw materials were processed into macaroni. Interchange of the two gluten fractions resulted in the largest quality differences. Starch interchange had no effect on the cooking water residue and only a limited effect on the cooked weight.

By means of model pasta (consisting of a blend of a starch and gluten), Frey (1970) investigated the role of

starch and proteins. Starches of varying botanical origin in the model pasta had a large influence on its consistency. Wheat and maize starches yielded the best pastas; the use of rice, tapioca, and certainly waxy maize starches was detrimental. Incorporation of severely cross-linked wheat starch in the model pasta yielded a porridge after cooking, suggesting that the gelatinization properties of starch are of crucial importance for good cooking quality. Frey (1970) found only a very limited (if any) correlation between cooking quality and the gelatinization temperature, granule size distribution, or swelling power of the used starches (of varying botanical origin). However, the differences in consistency of the model pastas reflected the characteristics of concentrated gels, made by gelatinization of the respective starches in the absence of mechanical stress.

The importance of starch in general and amylose in particular for pasta quality was illustrated by Dexter and Matsuo (1979). Starches of different botanical origin were mixed with durum semolina gluten. With decreasing amylose content in the reconstituted samples, cooking quality deteriorated. In contrast, when the proportion of amylose increased, the cooked pasta became slightly firmer. However, with starches of varying botanical origin, it was found that, above a certain threshold level of amylose, other starch properties may supersede amylose content in imparting superior cooking quality.

Nelson (1982) added modified commercial and durum starches in varying amounts (up to 10%) to pasta blends. Spaghetti diameter, color, and cooking loss were not affected by any of the added starches. The commercial starches decreased the optimum cooking times by 1–2 min, possibly due to the lower protein levels after starch

\* To whom correspondence should be addressed. Phone: +32.(0)16.32.16.34. Fax: +32.(0)16.32.19.97. E-mail: jan.delcour@agr.kuleuven.ac.be.

<sup>†</sup> Katholieke Universiteit Leuven.

<sup>‡</sup> INRA.

<sup>§</sup> E-mail: abecassi@ensam.inra.fr.

<sup>||</sup> Agricultural State University.

addition. In contrast with the modified durum starches, addition of the commercial starches to the samples had a significant effect on firmness and cooked weight.

The relative importance of starch and amylose was assessed with a multiple variance analysis (D'Egidio et al., 1983). In pasta, amylose was responsible for 37% of the pasta quality. It was further suggested that a better finished product is obtained if less starch is damaged during pasta processing.

Dalbon et al. (1985) prepared reconstituted durum wheat pasta by mixing the gluten with starches that were dried with different drying profiles. Starches dried at low temperature produced the worst spaghetti; starches that were exposed to high temperatures at low humidity yielded reconstituted pasta of increased quality. These results suggest that those starch properties that can be changed by a heat-moisture treatment play a role in pasta quality.

Some work has also been done on the interactions between starch and other wheat components. However, only few studies show the influence of these interactions on pasta quality. According to D'Egidio et al. (1984), amylose binds to a protein fraction and, in this way, contributes to the formation of a protein network that avoids amylose-leaching during pasta cooking. Also, for some wheats, an increase in the protein fraction interacting with starch rather than an increase in protein content itself (D'Egidio et al., 1984) leads to improved pasta qualities.

Finally, Vansteelandt and Delcour (1998) found that the first drying steps of an industrial pasta production render the starch granules in general and the small ones in particular less extractable, possibly due to increased physical inclusion or interaction between starch and gluten components. Other production steps had much less impact on the interaction behavior.

It is clear that the role of starch and the interactions between durum semolina components have not been studied as extensively as have protein factors. Indeed, the role of starch and the interactions between starch and other components in pasta-making are not well-defined. More work is thus necessary to better understand protein-starch interactions and their influence on processing properties and product quality.

In what follows, fractionation and reconstitution experiments were carried out to provide insight into the role of starch and more specifically of its interactions with other semolina components in pasta quality. As Kulp (1973) described that wheat starch-wheat protein interactions were different in starch-gluten doughs made from small or regular wheat starch granules, we investigated the influence of granule size distribution toward interaction behavior and pasta quality. Furthermore, because starch surface properties are important for starch (Eliasson et al., 1981; Segushi, 1993) and starch interaction behavior (Lindahl and Eliasson, 1986; Bushuk, 1988), starch was treated to remove surface proteins and lipids prior to use in reconstitution experiments.

## MATERIALS AND METHODS

**Semolina Fractionation.** Commercial durum wheat semolina was obtained from N.V. Soubry (Roeselare, Belgium). Semolina (46 kg) was mixed in batches of 2.0 kg each (as is) in a Hobart A200 mixer equipped with a dough hook with 1.2 L of water (room temperature) for 3 min (speed 1) and 5 min (speed 2). Each resulting dough was allowed to rest for 8 min.

Water (2.0 L) was then added, and the dough was stirred with a flat beater for 20 min. The mixture was then diluted with 2.0 L of water and poured over vibrating sieves with decreasing pore size (400, 250, 125, and 90  $\mu\text{m}$ , respectively). The protein fraction was recovered from all sieves. The filtrates were centrifuged (1800g, 10 min, room temperature), and supernatant was collected as a water-extractable fraction. The sediment consisted of a yellow-brown layer of sludge fraction with a starch layer underneath. The latter was resuspended in water and centrifuged a second time. The top layer was scraped off as a sludge fraction; the white bottom layer was collected as a starch fraction and was air-dried at room temperature. It is further referred to as SF. All other fractions were frozen with liquid nitrogen and lyophilized in an industrial facility (Lyobel, Boortmeerbeek, Belgium) and are further referred to as PF (protein fraction), WEF (water-extractable fraction), and SLF (sludge fraction).

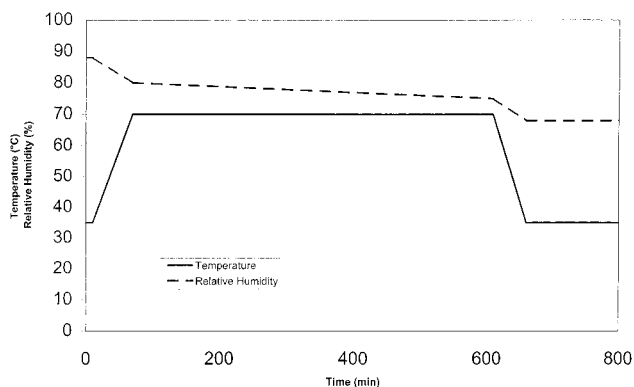
**Fraction Characterization.** Protein contents were determined according to AACC Method 46-11A ( $N \times 5.7$ ) (AACC, 1995). Moisture contents were determined by analyzing the weight loss of 3.0 g of accurately weighed sample after 90 min at 130 °C. Sugar compositions were determined by gas chromatography of alditol acetates obtained after hydrolysis (120 min at 110 °C), reduction, and derivatization as described by Englyst and Cummings (1984). The derivatives were separated on a Supelco (Bellefonte, PA) SP-2380 column (30 m, 0.32  $\mu\text{m}$  i.d., 0.2 mm film thickness) in a Chrompack 9011 chromatograph (Middelburg, The Netherlands) equipped with a flame ionization detector. The carrier gas was He. Separation was at 225 °C, with injection and detection temperatures of 275 °C. The internal standard was  $\beta$ -D-allose (Sigma, Bornem, Belgium). The sugar composition results were used to calculate starch and arabinoxylans (AX) contents in the samples. Starch content was calculated as glucose content  $\times$  0.9 and AX content as the sum of xylose and arabinose (corrected for its occurrence in arabinogalactans; Loosveld et al., 1997) contents multiplied by 0.88.

**Starch Modifications.** *Starch Surface Defatting.* Methanol (80%) was added to SF (w/v, 1:3). The suspension was shaken continuously for 120 min at room temperature, Buchner-filtered, and washed three times with 1.5 L of 80% methanol. The starch was washed exhaustively with water and air-dried. It is further referred to as DF. Thin-layer chromatography with flame ionization detection was performed on the 80% MeOH extract of the starch fraction to assess semiquantitatively the amounts of the three main classes of starch lipids (lysophospholipids, free fatty acids, and monoacylglycerols) removed (De Schrijver and Vermeulen, personal communication).

*Starch Surface Protein Removal.* SF was shaken for 120 min at room temperature with a solution (w/v = 1/2) containing 0.1% dithiothreitol and 0.1% acetic acid. The obtained deproteinized starch was Buchner-filtered, washed exhaustively with water, and air-dried. It is further referred to as DP.

*Starch of Changed Granule Size Distribution.* SF was suspended in water, centrifuged gently (1800g, 10 min, room temperature), and separated into top [enriched in small (ca. 5  $\mu\text{m}$ ) granules] and bottom [enriched in large (ca. 15  $\mu\text{m}$ ) granules] layers (Vansteelandt and Delcour, 1998). By repeating this procedure and combination of the obtained layers, a starch fraction enriched in small granules (SM) and a fraction enriched in large granules (LA) were obtained.

**Starch Gelatinization Characteristics.** Starches were characterized by means of differential scanning calorimetry (DSC) and rapid visco analysis (RVA), as described before (Vansteelandt and Delcour, 1998). A Seiko DSC-120 (Kawasaki Kanagawa, Japan), using ca. 5 mg of accurately weighed starch and adding water to obtain a ratio of 1:2 (w/w), was used. We heated the starches from 20 to 150 °C at 4 C/min and carried out all experiments at least in triplicate. The RVA 3d (Newport Scientific, Sydney, Australia) was operated with 25.0 g of 9.9% starch-in-water suspensions. The temperature profile included a 2 min isothermal step at 50 °C, a linear temperature increase to 95 °C in 7 min, a holding step (8 min at 95 °C), a cooling step (7 min) with a linear temperature decrease to 50 °C, and



**Figure 1.** Drying diagram (temperature and relative humidity in the dryer as a function of time) used to reduce the moisture content of all pasta samples to ca. 12.5%.

a final isothermal step at 50 °C. Duplicate measurements always agreed within 5 rapid visco units over the whole profile.

**Reconstitution.** All fractions (except for WEF) were ground with a Cyclotec 1093 sample mill (Tecator, Sweden) prior to reconstitution (i.e., recombination of all different fractions taking into account their respective yields) to improve the homogeneity of the reconstituted product. Samples were reconstituted to a powdery farina with the original yield of each fraction as a basis and rehydrated to 10–12% moisture as described elsewhere (Sheu et al., 1967). WEF was not added to the reconstituted farina, but the appropriate amounts were dissolved in water prior to addition during pasta-making (cf. *infra*).

**Pasta Production and Samples.** The reconstituted farina (Re-pasta) and original semolina (Se-pasta) samples were transformed into spaghetti (diameter of the dried pasta 1.45 mm) using a Mini Press (Sercom, Montpellier, France). An additional pasta sample (SeLD) was made from a farina obtained by grinding a lyophilized dough. The dough was made as described above (2.0 kg of semolina + 1.2 L of water, Hobart mixer) from the original commercial durum wheat semolina. This farina and the control semolina (ca. 800 g) were hydrated to 52% (dry matter base) using deionized water. The reconstituted farinas were hydrated to the same moisture level with deionized water containing the WEF. The water was added slowly (5 min) during the first 15 min of blending. The dough was then allowed to rest for 5 min and mixed for 5 min more. Extrusion of the samples was at 36 °C under a pressure of ca. 9.5 MPa and under partial vacuum. Pasta was dried to about 12.5% moisture using a cycle at 70 °C (see Figure 1). Samples were stored at 20 °C for at least 4 days before analysis.

For comparison, a commercial spaghetti (CSp) with a diameter of 1.45 mm ("spaghetti fijn extra", Soubry, Roeselare, Belgium) was also included in this study.

**Pasta Quality Assessment.** *Color.* Brown, red, and yellow indices were determined on the dry, uncooked pasta products with a Minolta CR310 (Minolta, Osaka, Japan) colorimeter.

*Pasta Cooking.* Spaghetti strands (50 g), broken to a length of ca. 15 cm, were cooked into 1.5 L of salted (7.0 g/L) mineral water (as recommended by AFNOR Standard NF-V 03-714). The minimum cooking time ( $T$ ) was defined as that needed to gelatinize starch at the center of spaghetti strands as evaluated by visual inspection. Cooking was then continued for 1 ( $T + 1$ ), 6 ( $T + 6$ ), and 11 ( $T + 11$ ) min.

*Evaluation of the Surface Condition.* For surface condition evaluation, pasta strands were allowed to drain for 3 min in a colander at  $T + 6$  and  $T + 11$  min. Scores between 1 and 9 (1 = very bad, 9 = excellent) were then given by a panel with photographs as a reference as outlined by Autran et al. (1986). The general appearance, degree of swelling, and stickiness were taken into account for assessment of the overall score.

*Firmness of the Cooked Pasta.* The firmness of the pasta was assessed with the viscoelastograph (Chopin, Paris, France). At  $T + 1$ ,  $T + 6$ , and  $T + 11$  min, five strands of pasta were removed from the cooking water and stored in Petri dishes

under a water-saturated atmosphere until measurement. Measurements were performed on the strands cut at 2.0 cm length. The initial thickness ( $t_1$ ), the thickness ( $t_2$ ) after the strand was crushed for 40 s under a load of 500 g, and the thickness ( $t_3$ ) 20 s after release of the load were assessed. From the obtained mean values, the compressibility  $C = (t_3 - t_1)/t_1$  and the relative recovery  $R = (t_2 - t_1)/(t_3 - t_1)$  were calculated. A viscoelasticity index (VI) was then calculated from these results as  $VI = R/C \times 10$ , with a low or high score representing soft or firm pasta, respectively (Autran et al., 1986).

*Water Absorption and Losses during Cooking.* Pasta (30.0 g) was cooked in 1.5 L of tap water for  $T + 11$  min. Samples were drained for 1 min and weighed. Water absorption was calculated as the weight increase and expressed as a percentage of the sample weight (as is) before cooking. Cooking loss was determined gravimetrically following mixing of the recovered and volumetrically measured cooking water with an Ultra-Turrax for 1 min and evaporation and drying of 25.0 mL of this dispersion at 105 °C for 150 min.

**Starch Interaction Behavior.** Starch isolation was done with a batter isolation method described previously (Vansteelant and Delcour, 1998). The granule size distribution was analyzed using a Coulter Multisizer II (Coulter Electronics Ltd., Luton, England) equipped with a 140  $\mu$ m aperture tube and measuring in 256 channels. Due to large background noise for small particles, the measuring range was only between 4.3 and 84  $\mu$ m. The equipment was calibrated with polystyrene divinylbenzene latex. Starch samples were dispersed in sodium chloride solution (5.0 g/L).

**Statistical Relevance of the Pasta Analytical Data.** All pasta samples were produced at least in duplicate and analyzed for color scores (also at least in duplicate). Moreover, at least two cooking tests were performed for each sample produced, and all analyses of all cooked samples were again at least in duplicate. The results are reported as averages of the analytical data with the corresponding pooled standard deviations.

## RESULTS AND DISCUSSION

**Fraction Characterization.** Table 1 lists the yields of the fractions and their relative compositions as well as those of the semolina. Mass balances indicate that the starch yield was somewhat higher and that the protein and AX yields were somewhat lower than present in the starting material. In a smaller scale fractionation, Sheu et al. (1967) also obtained a lower protein recovery.

The SF was rather pure. Only 0.5% proteins were present, and no AX could be detected. The highest AX concentration was found in the WEF. Taking into account the relative yields of the fractions, most AX were found in the PF and SLF.

**Starch Characterization.** *Influence of Surface Defatting and Surface Protein Removal.* The three main classes of starch lipids (lysophospholipids, free fatty acids, and monoacylglycerols) were found in the extract with relative ratios of 6.8:2.3:1, respectively. Semiquantitative estimation showed that the surface lipid extraction yield was certainly higher than 0.2 mg/g of starch, comparable with results presented by Eliasson et al. (1981) for wheat starch.

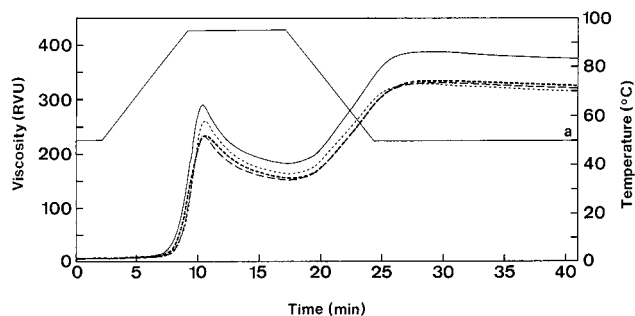
From Figure 2, it is clear that surface defatting does not significantly affect starch viscosity behavior, except for a somewhat higher swelling peak viscosity. Surface protein removal, even when the protein level in the (nondeproteinized) starch was only 0.5%, induces this effect much more. Apparently, DP swells more during gelatinization and pasting, but is less stable after swelling. As a consequence, the setback viscosity is comparable to that of SF. The higher granule swelling



**Table 1. Moisture, Starch, Protein, and AX Contents of Analytes**

fraction <sup>a</sup>	moisture content (%) <sup>c</sup>	starch content <sup>b</sup> (%) <sup>c</sup>	protein content (%) <sup>c</sup>	AX content <sup>b</sup> (%) <sup>c</sup>	relative yield (%)
semolina	15.5	67.9	14.6	2.0	
SF	13.8	85.7	0.5	0.0	64.7
PF	3.9	49.1	41.6	5.4	25.9
SLF	3.4	73.7	19.6	3.3	8.5
WEF	8.7	50.8	32.8	7.7	0.9

<sup>a</sup> Abbreviations used: SF = starch fraction; PF = protein fraction; SLF = sludge fraction; WEF = water-extractable fraction. <sup>b</sup> The relative error on these values is generally lower, but can be as high as 10%. <sup>c</sup> Percentage expressed on as is base.



**Figure 2.** RVA diagrams of the starches at a concentration of 9.9%: (curve a) temperature profile; (---) original starch fraction; (- - -) surface defatted starch fraction; (- · -) surface deproteinized starch fraction; (- - -) starch fraction enriched in large granules.

can be explained by higher and/or faster water penetration into the starches. If so, our results concur with those of Segushi (1993), who illustrated that proteins rather than lipids control the hydrophobicity of and thus the water penetration into starch granules. Further work identifying the nature of the (limited levels of) durum proteins removed would certainly have been useful, but was beyond the scope of the present study.

Surface defatting but even more so surface protein removal induced a lower DSC gelatinization temperature of the starches (Table 2). It seems logical that the removal of a water diffusion barrier allows a faster water penetration and allows the starch to gelatinize at lower temperatures. Also, the starches may have lost salts during the removal procedures in which they were washed exhaustively with deionized water. Extensive desalting of rice starches decreases starch DSC gelatinization temperatures up to several degrees Celsius and significantly increases their RVA peak viscosities. The latter was also observed for wheat starch (Vermeylen and Vandeputte, personal communication).

**Influence of Changing the Granule Size Distribution.** Light microscopy pictures clearly showed the differences in granule size distribution among the SF, SM, and LA starches (results not shown). The RVA diagrams (Figure 2) show that starch enriched in large granules was more viscous after gelatinization. The viscosity onset temperature was also lower for this sample. Both these observations are similar with those of Kulp (1973). DSC results are presented in Table 2. It is known from the literature (Kulp, 1973; Eliasson and Karlsson, 1983) that small wheat starch granules gelatinize at higher temperatures than the large granules. Our results concur with this, except those of the onset temperature as observed in the DSC. Furthermore, in analogy with the present findings (Table 2), Knutson et al. (1982) and Vasanthan and Bhatta (1996) earlier reported  $T_c - T_0$  to be larger for small-granule than for large-granule starch. The higher enthalpy values of the amylose-lipid endothermic transition ( $\Delta H^{\circ}$ ) for SM than that of LA can possibly be explained in terms of a higher lipid

content in the small-granule starch (Kulp, 1973; Eliasson and Karlsson, 1983; Vasanthan and Bhatta, 1996).

**Pasta Production.** As illustrated in Table 3, commercial semolina yielded, on a laboratory scale, pasta (Se) with characteristics comparable with those of commercial spaghetti (CSp). The surface condition, VI, water absorption, and cooking loss of the two pastas were very similar. However, the cooking time was 1 min longer for the CSp spaghetti.

**Visual Properties of the Pasta.** The dried pasta samples all much resembled industrially made pasta, except for the pasta made from the starch enriched in small granules (ReSM). The latter samples showed opalescent spots throughout the glassy strains.

Pasta made from the control semolina in general had the highest scores for brown, red, and yellow (Table 3). The SeLD sample had different color characteristics. The reconstituted samples all had very comparable color scores, indicating that the starch properties under study do not determine pasta color. However, values for ReSM are among the lowest, maybe because of its opalescent dots.

**Pasta Cooking Times.** Optimum cooking time depends primarily on the rates of water penetration and starch gelatinization. Water penetration is more rapid at lower protein levels (Nelson, 1982). The reconstituted samples had longer minimal cooking times than the pasta produced from semolina (Table 3). This is possibly due to differences in gluten properties and consequently ultrastructure. Indeed, during the (wet) fractionation procedure, a gluten network was developed prior to sieving, lyophilization, and milling. This may have had an impact on the physicochemical behavior of gluten in the reconstituted pasta samples, where the aggregated gluten may have formed a barrier to fast water penetration and consequently have been responsible for the higher minimal cooking time. This contrasts with properties of regular pasta, where it is believed that no fully developed gluten network exists. However, although the cooking time of SeLD was longer than for Se, it was shorter than for ReSF (Table 3). Other factors are thus also in play. Perhaps, as during the fractionation procedure the semolina components were in aqueous surroundings for several hours at room temperature, enzymes may have changed semolina constituent properties. It is also of note that the cooking time of the commercial spaghetti sample (CSp) is comparable to that of the reconstituted samples and higher than that of the Se sample.

**Pasta Surface Condition.** The reconstituted samples had higher surface condition quality scores than both the sample made from semolina and the commercial one (Table 3). The gluten properties in the reconstituted samples (cf. supra) are not believed to be responsible for this. Indeed, comparison of all reconstituted samples with the SeLD sample clearly shows that the changed gluten properties are, at most, only partially responsible for the better pasta surface condition.

**Table 2. Average DSC Gelatinization Onset ( $T_o$ ), Peak ( $T_p$ ), and Conclusion ( $T_c$ ) Temperatures, Gelatinization Intervals ( $T_c - T_o$ ), Gelatinization Enthalpies ( $\Delta H^1$ ), and Enthalpies of the Melting of Amylose-Lipid Complexes ( $\Delta H^2$ ) of Native and Modified Starches<sup>a</sup>**

sample <sup>b</sup>	$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)	$T_c - T_o$ (°C)	$\Delta H^1$ (J/g)	$\Delta H^2$ (J/g)
SF	50.2 (0.5)	58.5 (0.3)	65.9 (0.5)	15.7	12.2 (1.6)	1.8 (0.1)
DF	49.6 (1.3)	58.1 (0.1)	63.5 (0.7)	13.9	12.1 (1.1)	1.7 (0.2)
DP	48.3 (0.5)	57.6 (0.1)	62.6 (0.8)	14.3	11.1 (3.1)	2.2 (0.2)
SM	47.1 (1.9)	58.4 (0.2)	64.6 (1.2)	17.5	11.0 (1.6)	2.3 (0.2)
LA	49.3 (0.2)	57.7 (0.4)	62.8 (0.9)	13.5	10.1 (2.5)	1.9 (0.2)

<sup>a</sup> All values are averages of at least triplicate measurements with standard deviations in parentheses. <sup>b</sup> Abbreviations used: SF = starch fraction; DF = surface defatted starch; DP = starch with surface proteins removed; SM = starch enriched in small granules; LA = starch enriched in large granules.

**Table 3. Average Color Scores, Minimal Cooking Times ( $T$ ), Surface Conditions, Viscoelasticity Indices, Cooking Weights, and Cooking Losses of the Samples<sup>a</sup>**

description of the sample <sup>b</sup>	color scores			$T$ (s)	surface condition			viscoelasticity index				water absorption (%)	cooking loss (%)
	brown	red	yellow		$T+6$	$T+11$	av	$T+1$	$T+6$	$T+11$	av		
Se	42.0 (0.2)	2.3 (0.2)	33.5 (0.2)	390 (0)	5.9 (0.1)	4.6 (0.4)	5.3	5.9 (0.5)	5.8 (0.2)	5.0 (0.5)	5.6	268.2 (3.4)	10.8 (0.1)
ReSF	40.2 (0.1)	2.2 (0.2)	31.1 (0.2)	454 (27)	7.3 (0.4)	6.9 (0.6)	7.1	13.0 (0.8)	9.6 (0.7)	6.0 (0.5)	9.5	298.6 (0.3)	8.8 (0.2)
SeLD	43.6 (0.7)	0.7 (0.4)	32.7 (1.1)	432 (16)	6.3 (0.3)	5.7 (0.4)	6.0	5.7 (0.5)	5.5 (0.6)	4.3 (0.2)	5.2	270.5 (5.9)	14.2 (0.5)
CSp	nd <sup>c</sup>	nd <sup>c</sup>	nd <sup>c</sup>	450 (0)	5.3 (0.4)	4.5 (0.4)	4.9	7.9 (1.2)	6.6 (0.3)	3.7 (0.9)	6.1	267.2 (8.9)	10.2 (0.7)
ReDF	40.5 (0.1)	2.2 (0.1)	30.4 (0.1)	450 (24)	6.9 (0.4)	6.5 (0.5)	6.7	12.9 (1.2)	9.6 (1.2)	5.3 (0.9)	9.3	300.4 (5.1)	8.5 (0.4)
ReDP	40.6 (0.2)	1.9 (0.2)	30.1 (0.1)	480 (0)	7.0 (0.1)	6.5 (0.2)	6.7	13.3 (0.7)	9.1 (0.4)	5.6 (0.5)	9.3	301.8 (3.5)	8.7 (0.4)
ReSM	40.2 (0.1)	2.0 (0.0)	29.7 (0.0)	450 (0)	6.7 (0.1)	6.2 (0.3)	6.4	13.7 (0.3)	9.5 (0.5)	6.2 (0.6)	9.8	297.8 (5.6)	9.1 (1.3)
ReLA	40.5 (0.3)	1.9 (0.1)	30.3 (0.1)	465 (17)	7.3 (0.1)	6.8 (0.4)	7.1	13.8 (1.0)	8.7 (0.5)	5.6 (0.6)	9.4	304.2 (4.9)	8.4 (0.8)

<sup>a</sup> Where appropriate, pooled standard deviations are represented in parentheses. <sup>b</sup> Abbreviations used: Se = semolina; Re = reconstituted sample; SF = starch fraction; LD = lyophilized dough; CSp = commercial spaghetti; DF = surface defatted starch; DP = starch with surface proteins removed; SM = starch enriched in small granules; LA = starch enriched in large granules. <sup>c</sup> nd = not determined.

It is further of note that the pasta with a relatively higher content of smaller starch granules had the lowest surface condition, maybe due to the opalescent dots at its surface.

**Pasta Firmness.** When comparing Se (and Csp) for firmness (Table 3) with the reconstituted samples, we again recognize the latter samples as the best. All reconstituted samples had a much higher VI, indicating firmer samples with a larger recovery after compression (Autran et al., 1986). However, the large differences in VI between the pasta made from semolina and the reconstituted pastas that was noticed at  $T+1$  was much smaller at  $T+6$  and almost disappeared at  $T+11$ , indicating that the reconstituted samples were much more sensitive to overcooking than the Se sample. The very low VI scores for the SeLD sample indicate that the higher quality of the reconstituted samples is not due to the changed gluten properties in these samples. As described above, enzymatic activity during fractionation may have changed semolina constituent properties.

From Table 3 it also follows that neither starch surface properties nor starch granule size distribution has an important influence on pasta firmness, recovery, and cooking resistance. Frey (1970) also found no correlation between granule size distribution and pasta tensile strength. As starch surface properties seem to be unimportant for the observed pasta quality, the same can be said about the surface-mediated interactions between starch and other semolina components. With the changed starch surface characteristics and changed granule size distributions, the gelatinization behavior of the starches was also (slightly) changed (Table 2 and

Figure 2). It can therefore equally be concluded from Table 3 that, under the experimental conditions of the present work, those aspects of starch gelatinization that are influenced by removal of lipids or proteins, or by changes in granule size distribution, do not influence pasta firmness.

#### Water Absorption and Losses during Cooking.

The Se and CSp samples can again be discerned from the Re samples for water absorption and losses during cooking (Table 3). It seems that samples prepared from semolina have lower water absorptions and higher cooking losses than Re samples. The changed gluten properties in the reconstituted samples are not responsible for this, as evidenced by the low water absorption and the very high cooking loss of the SeLD sample.

No clear differences can be discerned between the reconstituted samples, except for ReSM, which had a somewhat higher cooking loss.

**Starch Interaction Behavior.** The starch yield (percentage of dry starch isolated out of pasta as is) obtained out of the pasta made from semolina (42%) was higher than with the reconstituted samples (average 33%). The standard deviation on starch yields for each sample was always smaller than 2%. The granule size distributions of starch isolated out of semolina and starch isolated out of pasta made from that semolina were almost equal. This is in contrast with all reconstituted samples, where much less small granules were isolated out of the pastas (results not shown). The lower starch yield for the reconstituted samples and the fact that less small starch granules could be isolated from them suggests (Vansteelandt and Delcour, 1998) the existence of stronger starch-gluten interactions or

stronger physical inclusion of the starch in the gluten network when the gluten had been in contact with an excess of water during the isolation procedure.

Starch was more easily isolated out of ReLA (37%) than out of ReSM (27%). As the isolation method comprised a centrifugation step and large starch granules sediment more rapidly from water (Reddy and Seib, 1999), this difference in isolation yield is thought not to result from their different interaction behavior, but more likely from their different shape during centrifugation.

Also, no differences in starch isolation yields could be found for the samples ReSF, ReDF, and ReDP (34%, 33%, and 34%, respectively), indicating that starch surface properties do not influence the starch interaction behavior in the raw pasta, and that the proteins and lipids removed during the starch treatment steps have no influence on the interaction between gluten and starch. From this, it is reasonable to conclude that starch interaction behavior in uncooked pasta is mainly by physical inclusion. This concurs with Saulnier et al. (1997) and Roels et al. (1998), who recently showed that most of the polysaccharide associated with wheat gluten is physically entrapped in the gluten network.

## CONCLUSIONS

The fractionation and reconstitution methodology used in this work influences the starch interaction behavior and the quality of pasta. Reconstituted pastas have increased starch interactions (physical inclusion), lower color scores, longer minimum cooking time, better surface quality, higher VI, larger sensitivity to overcooking, higher water absorption, and lower cooking losses than pasta made from semolina. This contrasts with the reconstitution of bread flours, where it is possible to make bread from recombined flours that is equal to that made with the original, nonfractionated flour (Finney, 1943). Because bread doughs contain more water than pasta doughs, it is not logical that the wheat or durum wheat fractionation process (which occurs in excess water and precedes the reconstitution process) is more compatible with the conditions in bread-making than with those in pasta-making.

Gluten aggregation during the fractionation procedure was not responsible for the observed changes in  $T$ , surface condition, VI, water absorption, and cooking loss. Other factors must be in play. Perhaps, enzymatic activity during the fractionation procedure may have changed the semolina constituent properties.

Starch surface lipid and protein removal clearly affects the starch DSC and RVA properties, but not the starch interaction behavior. The surface characteristics thus seem to be of little importance for the starch interaction behavior, implying that gluten–starch interaction in raw pasta is mainly due to physical inclusion of starch in the gluten network. High-temperature drying promotes the coagulation of protein fractions into a continuous network (Resmini and Pagani, 1983; Pagani et al., 1986) that renders the starch granules less extractable (Vansteelandt and Delcour, 1998) and restricts their gelatinization and swelling during cooking. Consequently, the quality and quantity of this network correlate with the physical properties of the cooked pasta (Resmini and Pagani, 1983). In this context, it is easy to understand that all reconstituted pasta samples had generally the same cooking quality. From

the latter, it must also be concluded that the slight changes in starch gelatinization behavior that are caused by the starch modifications (lipid removal/deproteination/changed granule size distribution) are of little importance for pasta quality.

## ABBREVIATIONS USED

AX, arabinoxylans; CSp, commercial spaghetti; DF, surface defatted starch;  $\Delta H^1$ , gelatinization enthalpy;  $\Delta H^2$ , enthalpy of the melting of amylose–lipid complexes; DP, surface deproteinized starch; DSC, differential scanning calorimetry; LA, starch enriched in large granules; LD, lyophilized dough; PF, protein fraction; Re, pasta made from reconstituted farina; RVA, rapid visco analysis; Se, pasta made from semolina; SF, starch fraction; SLF, sludge fraction; SM, starch enriched in small granules;  $T$ , minimum cooking time;  $T_c$ , conclusion temperature of gelatinization;  $T_o$ , onset temperature of gelatinization;  $T_p$ , peak temperature of gelatinization; VI, viscoelasticity index; WEF, water-extractable fraction.

## ACKNOWLEDGMENT

Etn. Joseph Soubry N.V. (Roeselare, Belgium) is thanked for supplying the semolina, S. Verhaeghe is thanked for the interaction behavior experiments, R. De Schrijver and D. Vermeulen (this university) are thanked for the lipid analysis, J. Ingelbrecht (this laboratory) is thanked for helpful discussions, and Amylum N.V. (Aalst, Belgium) is thanked for the use of the Coulter Multisizer II.

## LITERATURE CITED

- AACC (American Association of Cereal Chemists). *Approved Methods of the AACC*, 9th ed.; AACC: St. Paul, MN, 1995.
- Autran, J. C.; Abécassis, J.; Feillet, P. Statistical evaluation of different technological and biochemical tests for quality assessment in durum wheats. *Cereal Chem.* **1986**, *63*, 390–394.
- Bushuk, W. Protein–lipid and protein-carbohydrate interactions in flour-water mixtures. In *Chemistry and Physics of Baking*; Blanshard, J. M. V., Frazier, P. J., Galliard, T., Eds.; Royal Society of Chemistry: London, 1988.
- Dalbon, G.; Pagani, M.; Resmini, P.; Lucisano, M. Einflüsse einer Hitzebehandlung der Weizenstärke während des Trocknungsprozesses (Impact of wheat starch thermal treatment during the pasta drying process). *Getreide, Mehl Brot* **1985**, *39*, 183–189.
- D'Egidio, M. G.; De Stefanis, E.; Fortini, S.; Galterio, G.; Mariani, B. M.; Nardi, S.; Sgrulletta, D.; Volpi, M. Untersuchung der an die Qualität der Teigwaren gebundenen Eigenschaften—Veränderungen in der Stärkezusammensetzung während der Herstellung und des Kochens der Teigwaren (Research into factors governing pasta quality—changes in starch composition during production and cooking of pasta products). *Getreide, Mehl Brot* **1983**, *37*, 55–60.
- D'Egidio, M. G.; De Stefanis, E.; Fortini, S.; Nardi, S.; Sgrulletta, D. Interaction entre l'amidon et une fraction protéique extraite des semoules de *T. durum* (Interaction between starch and a protein fraction extracted from *T. durum* semolina). *Can. J. Plant Sci.* **1984**, *64*, 785–796.
- Dexter, J. E.; Matsuo, R. R. Effect of starch on pasta dough rheology and spaghetti cooking quality. *Cereal Chem.* **1979**, *56*, 190–195.
- Eliasson, A.-C.; Carlson, T. L.-G.; Larsson, K.; Miezi, Y. Some effects of starch lipids on the thermal and rheological properties of wheat starch. *Starch/Stärke* **1981**, *33*, 130–134.



- Eliasson, A.-C.; Karlsson, R. Gelatinisation properties of different size classes of wheat starch granules measured with differential scanning calorimetry. *Starch/Stärke* **1983**, *35*, 130–133.
- Englyst, H. N.; Cummings, J. N. Simplified method for measurement of total nonstarch polysaccharides by gas-liquid chromatography of constituent sugars as alditol acetates. *Analyst* **1984**, *109*, 937–942.
- Finney, K. F. Fractionation and reconstituting techniques as tools in wheat flour research. *Cereal Chem.* **1943**, *20*, 381–396.
- Frey, A. Untersuchungen an Modellteigwaren (Research on model pasta systems). Thesis, Eidgenössischen Technischen Hochschule Zürich, Switzerland, 1970.
- Knutson, C. A.; Khoo, U.; Cluskey, J. E.; Inglett, G. E. Variation in enzyme digestibility and gelatinization behavior of corn starch granule fractions. *Cereal Chem.* **1982**, *59*, 512–515.
- Kulp, K. Characteristics of small-granule starch of flour and wheat. *Cereal Chem.* **1973**, *50*, 666–679.
- Lindahl, L.; Eliasson, A.-C. Effects of wheat proteins on the viscoelastic properties of starch gels. *J. Sci. Food Agric.* **1986**, *37*, 1125–1132.
- Loosveld, A.-M.; Grobet, P. J.; Delcour, J. A. Contents and structural features of water-extractable arabinogalactan in wheat flour fractions. *J. Agric. Food Chem.* **1997**, *45*, 1998–2002.
- Nelson, J. M. Modification of starch and its effect on pasta quality. Thesis, North Dakota State University, Fargo, ND, 1982.
- Pagani, M. A.; Gallant, D. J.; Bouchet, B.; Resmini, P. Ultrastructure of cooked spaghetti. *Food Microstruct.* **1986**, *5*, 111–129.
- Preston, K. R. Protein-carbohydrate interactions. In *Interactions: the Keys to Cereal Quality*; Hamer, R. J., Hosney, R. C., Eds.; American Association of Cereal Chemists: St. Paul, MN, 1998.
- Reddy, I.; Seib, P. A. Paste properties of modified starches from partial waxy wheats. *Cereal Chem.* **1999**, *76*, 341–349.
- Resmini, P.; Pagani, M. A. Ultrastructure studies of pasta. A review. *Food Microstruct.* **1983**, *2*, 1–12, 98.
- Roels, S. P.; Grobet, P. J.; Delcour, J. A. Distribution of carbohydrates in gluten fraction isolated from European wheats (*Triticum aestivum* L.) in a batter system. *J. Sci. Food Agric.* **1998**, *46*, 1334–1343.
- Sandstedt, R.; Schaumburg, L.; Fleming, J. The microstructure of bread and dough. *Cereal Chem.* **1954**, *31*, 43–49.
- Saulnier, L.; Andersson, R.; Åman, P. A study of the polysaccharide components in gluten. *J. Cereal Sci.* **1997**, *25*, 121–127.
- Seguchi, M. Contribution of wheat starch granule hydrophobicity to pancake texture. *Cereal Foods World* **1993**, *38*, 493–497.
- Sheu, R.-Y.; Medcalf, D. G.; Gilles, K. A.; Sibbitt, L. D. Effect of biochemical constituents on macaroni quality. I.-Differences between hard red spring and durum wheats. *J. Sci. Food Agric.* **1967**, *18*, 237–239.
- Vansteelandt, J.; Delcour, J. A. Physical behavior of durum wheat starch (*Triticum durum*) during industrial pasta processing. *J. Agric. Food Chem.* **1998**, *46*, 2499–2503.
- Vasanthan, T.; Bhatta, R. S. Physicochemical properties of small- and large-granule starches of waxy, regular, and high-amylose barleys. *Cereal Chem.* **1996**, *73*, 199–207.

Received for review September 27, 1999. Revised manuscript received April 26, 2000. Accepted May 4, 2000. J.V. acknowledges the receipt of a scholarship from the Vlaams Instituut voor de Bevordering van het Wetenschappelijk-Technologisch Onderzoek in de Industrie (Brussels).

JF991051M