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The impact of the protein network on the pasting and cooking properties of dry pasta products

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ABSTRACT

Durum wheat semolina gluten and starch as well as processing conditions determine pasta cooking quality. This study investigated whether, for good organoleptic properties, a permanent protein network needs to be formed during pasta drying or can still be formed during cooking. The cooking quality of 16 spaghetti samples was related to the levels of sodium dodecyl sulphate extractable protein (SDSEP), starch gelatinisation temperatures as well as to the swelling properties of milled dry spaghettis. SDSEP levels in dry and cooked products varied between 31% and 56%, and 12% to 21% of total protein contents, respectively. The highest quality spaghettis had relatively higher levels of SDSEP in the dry product, low starch gelatinisation temperatures and swelling powers, and rigid particles. The lowest quality spaghettis had lower levels of SDSEP and higher gelatinisation temperatures. This work implies that high pasta quality results from an optimal degree of protein polymerisation during drying and/or the subsequent cooking.

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1. Introduction

Pasta is consumed in large quantities throughout the world. Scientific research has been undertaken to understand the parameters influencing pasta processing and the final product quality. Ideally, cooked pasta is of *al dente* quality. It is firm and resilient with no surface stickiness and little if any cooking losses (Dexter, Matsuo, & Macgregor, 1985; Sissons, Ames, Hare, & Clarke, 2005; Troccoli, Borrelli, De Vita, Fares, & Di Fonzo, 2000; Wood, Batey, Hare, & Sissons, 2001). When one considers the durum wheat semolina based dry pasta production process and the subsequent cooking before final consumption, the choice of raw material and processing variables in the production of dry pasta are the only measures one can take to ensure the above cited *al dente* quality characteristics. In the choice of raw materials, the semolina particle size distribution, the protein content and quality, and the starch properties (level of damaged starch and swelling power) are important quality determining parameters (Cubadda, Carcea, Marconi, & Trivisonno, 2007; D'Egidio, Mariani, Nardi, Novaro, & Cubadda, 1990; Delcour, Vansteelandt, Hythier, & Abécassis, 2000a; Delcour et al., 2000b;

Dexter, Matsuo, & Morgan, 1983; Grant, Dick, & Shelton, 1993; Oak et al., 2006).

In the first stage of the production process following durum wheat milling, semolina is hydrated and transformed into dough particles which are extruded to generate continuous dough strands that are then dried. As a result of both mixing and extruding, starch granules are entrapped in an amorphous protein matrix (Dexter, Dronzek, & Matsuo, 1978; Resmini & Pagani, 1983). Although the main constituent of pasta by far is granular starch, at this stage of the process, it has no network forming ability (Cornell, 2004). The limited portion of damaged starch contains both amylose and amylopectin which takes up high levels of water and can form a transient network based on entanglement (Morrison, Tester, & Gidley, 1994). However, it is questionable whether damaged starch would be a major factor responsible for the network in dried pasta strands as pasta can also be made in the absence of such starch (Delcour et al., 2000a, 2000b).

This brings us to the network forming ability of gluten. Before drying at elevated temperatures, the glutenin component is (already) well suited to have formed networks in the extruded dough. These networks are transient as they arise from entanglement of the glutenin subunit based polymers as well as from dynamic thiol-disulfide exchange reactions (Veraverbeke & Delcour, 2002). It is hard to envisage that, at this stage of the process, the other gluten component, i.e. gliadin, would contribute to the network to any significant degree as it is of globular nature. Gliadin, however, determines the viscous properties of the gluten network.

Abbreviations: cP, centiPoise; dm, dry matter; DSC, differential scanning calorimetry; DTT, dithiothreitol; HT, high temperature; RVA, Rapid Visco Analyzer; SDSEP, sodium dodecyl sulphate extractable protein; SE-HPLC, size-exclusion high performance liquid chromatography; SP, swelling power.

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In the industry, drying cycles involving controlled high temperature (HT) technology have been introduced into pasta production (Pollini, 1996; Zweifel, Handschin, Escher, & Conde-Petit, 2003). Fairly HT (above 60 °C) and relative humidities (between 74% and 90%) can be applied at either the start of the drying phase with high product moisture (HM) (ca. 30%), or during the final stages of the drying phase at low product moisture (LM) (below 15%) (Resmini & Pagani, 1983; Zweifel et al., 2003). There are indications that HT–LM drying may be more effective in ensuring high firmness and low stickiness of cooked pasta (Baiano & Del Nobile, 2006; Dexter, Matsuo, & Morgan, 1981; Dexter et al., 1983; Zweifel et al., 2003). Elevated temperatures may cause protein disulfide cross-linking by oxidation of glutenin free sulfhydryl groups (Lagrain, Brijs, Veraverbeke, & Delcour, 2005; Lagrain, Thewissen, Brijs, & Delcour, 2008) leading to large protein polymers (Lamacchia et al., 2007). Under well specified conditions, i.e. temperatures exceeding 90 °C in a model system, glutenin links to gliadin through a sulfhydryl-disulfide exchange mechanism (Lagrain et al., 2008). Thus, it is reasonable to assume that, during HT drying, the proteins polymerise into a (partial) protein network in the raw/uncooked product, and that, under these specified conditions, the protein level would be more important than its quality in obtaining high quality pasta (D'Egidio et al., 1990; Novaro, D'Egidio, Mariani, & Nardi, 1993). Protein polymerisation as a result of drying can be monitored by measuring the contents of protein extractable in dilute sodium dodecyl sulphate (SDS) solution, i.e. SDSEP (Lagrain et al., 2005). The level of protein unextractable in such medium is then a measure for the degree of protein polymerisation.

During cooking, physical competition between starch swelling and properties of polymerised and polymerising proteins determines whether the final cooked pasta is firm and elastic (when a strong protein network is formed and starch particles are entrapped in this network) or rather sticky and soft (in the opposite case of significant starch swelling) (Delcour et al., 2000a, 2000b; Resmini & Pagani, 1983). From the above, it is clear that, during HT–LM drying, the continuous protein network, needed for a good cooking quality, is already formed in the raw pasta. This reduces and prevents the negative impact of starch swelling during cooking (Resmini & Pagani, 1983). In high quality pasta, this network remains continuous during cooking. According to Delcour et al. (2000a), its coherence is dictated by the way it withstands starch swelling. Starch swelling can indeed destroy the protein network during cooking. Substitution of semolina starch with waxy starch from different sources resulted in increased starch swelling properties, and a soft textured pasta (Gianibelli, Sissons, & Batey, 2005). Hence, the gluten component of pasta as well as its starch properties and processing conditions (especially the drying conditions) are of utmost importance for product quality. However, at present, apart from a pasta cooking test itself, there is no (predictive) analytical tool available which predicts pasta quality. Also, it is unclear whether the protein network needs to be formed already during industrial dry pasta production or can still be formed during the subsequent cooking step. In addition, little is known about the properties of this protein network and its effect on pasta quality.

Against this background, the cooking quality of 16 different commercial dry pasta products was determined and linked to the properties of starch (i.e. swelling) and proteins (i.e. network formation) during production and/or cooking of pasta. The study also used analytical approaches to determine the starch and protein properties which earlier on were used to unravel the impact of rice parboiling on the protein and starch components (Derycke et al., 2005). The swelling properties of ground uncooked pasta products were investigated using swelling power (SP) test and Rapid Visco Analyzer (RVA) heat-moisture-shear treatment. The impact of the protein component on the swelling power and rheological behav-

iour was estimated using a reducing agent. Furthermore, the levels of SDSEP in the uncooked and cooked pastas were determined. To the best of our knowledge, such work has, until now, not been reported in the literature.

2. Materials and methods

2.1. Materials

A set of 16 different dry spaghetti samples manufactured in Europe were purchased in a Belgian supermarket. In this study, five commercial non-heat treated durum wheat semolina samples served as control to have a good overall indication of the properties of the raw material that is used for pasta production. The diameter of all spaghettis was measured with a digital caliper. The mean diameter of each spaghetti sample was calculated from four measurements.

2.2. Chemicals and reagents

All used chemicals and reagents were at least of analytical grade and purchased from Sigma–Aldrich (Steinheim, Germany), unless specified otherwise.

2.3. Composition of semolina and uncooked pasta products

2.3.1. Analysis of moisture, starch and protein contents

All dry spaghettis were ground in a universal mill (IKA Labor-technik, Staufen, Germany) and sieved (<400 µm). Moisture contents were determined according to AACC Method 44-19 (AACC, 1983). Starch contents were estimated by gas–liquid chromatography of sorbitol acetate following starch hydrolysis, glucose reduction and derivatisation as described by Englyst and Cummings (1984) and was calculated as 0.9 times the glucose content. Starch damage was determined according to AACC Method 76-31. Protein contents were determined using the Dumas combustion method, an adaptation of the AOAC Official Method (AOAC, 1995) to an automated Dumas protein analysis system (EAS vario Max N/CN, Elt, Gouda, The Netherlands), using 5.7 as the conversion factor. Chemical analyses were performed in triplicate and the results are expressed on a dry matter (dm) basis.

2.3.2. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to determine the starch gelatinisation characteristics of uncooked ground pasta. It was performed with a DSC Q1000 (TA Instruments, New Castle, DE, USA). Milled spaghetti (ca. 5 mg dm) was accurately weighed into an aluminium sample pan and water was added (1:2 w/w dm/water). The sample pan and an empty reference pan were hermetically sealed and heated from 0 °C to 140 °C at 4.0 °C/min. Calibration was with indium and tin. The starch gelatinisation peak temperature (T_p , °C) of uncooked pasta samples was determined with TA Q Series Advantage Universal Analyses software (TA Instruments, New Castle, DE, USA). Semolina samples served as control. Results were reported as averages of at least three measurements.

2.4. Size-exclusion high performance liquid chromatography

Size-exclusion high performance liquid chromatography (SE-HPLC) was conducted using a Shimadzu LC-2010 system (Kyoto, Japan) with automatic injection. The milled dry and cooked spaghetti samples (corresponding to 1.0 mg dm proteins) were extracted with 1.0 ml sodium phosphate buffer (50 mM, pH 6.8) containing 2.0% (w/v) SDS (Acros Organics, Geel, Belgium) as well as with

1.0 ml of the same buffer containing 2.0% w/v SDS, 1.0% w/v dithiothreitol (DTT, Acros Organics, Geel, Belgium) and 2.0 M urea (Lagrain et al., 2005). The protein extracts were filtered through a 0.45 µm membrane (regenerated cellulose; Alltech Associates, Deerfield, MA, USA) and loaded (60 µl) on a Biosep-SEC-S4000 column (Phenomenex, Torrance, CA, USA). The elution solvent was acetonitrile/water (1:1, v/v) containing 0.05% (v/v) trifluoroacetic acid. Chromatography conditions included: flow rate 1.0 ml/min and temperature 30 °C (Veraverbeke, Larroque, Bekes, & Delcour, 2000), with protein detection at 214 nm. The elution profiles were divided into two fractions using the lowest absorbance reading between the two peaks as the cut-off point. Based on Lagrain et al. (2005), the first peak corresponds to the SDS extractable glutenin, while the second peak was assigned to the SDS extractable gliadin. Total SDSEP levels were calculated from the sum of the peak areas, and expressed as percentage of the peak area of total proteins extracted with the same phosphate buffer containing the above specified levels of SDS, DTT and urea.

In addition, semolina and spaghetti 1 and 16 were extracted before and after cooking with 2.0% (w/v) SDS containing sodium phosphate buffer (50 mM, pH 6.8) in the presence of different levels of DTT (0% w/v, 0.01%, 0.1%, 0.5%, 1.0%). The levels of proteins extractable in the different buffers were expressed as percentage of the peak areas of proteins extracted with 2.0% SDS sodium phosphate buffer (50 mM, pH 6.8) in the presence of 1.0% DTT and 2.0 M urea.

2.5. Cooking properties and spaghetti quality

2.5.1. Determination of optimal cooking time

Pasta products (25 g), broken to a length of 7 cm, were cooked in deionised water (400 ml). The optimal cooking time (*al dente* point) was that needed to gelatinise starch at the centre of spaghetti strands. It was visually determined by pressing such strands between two plastic plates at different times and measuring the time for the starchy white core of the pasta to disappear (Abécassis, Abbou, Chaurand, Morel, & Vernoux, 1994; Zweifel et al., 2003).

2.5.2. Cooking losses

Pasta products (25 g), broken to a length of 7 cm, were cooked in deionised water (400 ml) to optimal cooking time. To stop the cooking process, *al dente* cooked strands were immediately cooled in deionised water. Cooking and rinsing water were recovered quantitatively. The material leached to the cooking water was determined by weighing the freeze-dried cooking and rinsing water. Determination of cooking losses of the pasta products was reproducible as verified by three individual measurements for spaghetti 16 with a standard deviation (expressed in %) not exceeding 3.5%.

2.5.3. Water absorption of strands

Water absorption g/g dm was calculated by relating the weight increase between dry and cooked pasta to the dry matter content of dry pasta with correction for the cooking losses. Determination of water absorption of the pasta products was reproducible as verified by three individual measurements for spaghetti 16 with a standard deviation (expressed in %) not exceeding 1.5%.

2.5.4. Texture analysis

The texture of cooked spaghetti was determined using a TA-XT2i Texture Analyzer (Stable Micro Systems, Surrey, UK) using a 25 mm diameter flat-ended cylindrical probe (P/25, Stable Micro Systems). A single spaghetti strand was compressed 50% at a speed of 1.0 mm/s. At least nine subsequent compressions of a fresh strand from the same cook followed at 45 s intervals. The force at 50% compression was taken as a measure for the firmness (N)

of the spaghetti strands. The probe was then moved to its original position with the same speed. The negative peak value, originating from the force needed to remove the probe from the strand, was taken as a measure for the stickiness (mN) of the spaghetti strands. Evidently, thicker pasta requires more force to cut through the strands due to the greater cross-sectional area through which the knife must pass (Wood et al., 2001). To compare the texture of the different pastas, the firmness and stickiness were divided by the radius of the strands. This corresponds to the force by length unit at 50% compression (Dris & Niskanen, 1999).

2.6. Swelling properties

2.6.1. Swelling power

In order to determine the SP, i.e. the swelling power or the weight occupied by 1.0 g dm milled spaghetti after gelatinisation in excess water or buffer, a suspension (1.0% w/v) of milled spaghetti in TRIS–HCl buffer (100 mM, pH 7.0) was heated at 100 °C (30 min) and centrifuged (15 min, 1500g). The sediment was weighed and the SP (g/g) was calculated. The impact of proteins on SP and leaching behaviour was studied by including the reducing agent DTT (0.15%) into the buffer. The total carbohydrate contents of the supernatants were determined using the phenol–sulphuric acid method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956). All SP determinations were performed at least in triplicate.

2.6.2. Rapid Visco Analysis

Milled spaghetti pasting properties were determined with a Rapid Visco Analyzer (RVA-4D, Perten Instruments, Huddinge, Sweden) interfaced with a computer equipped with Thermocline software. Suspensions of dry milled spaghetti (12.0% w/v dm, total weight is 25.0 g) and TRIS–HCl buffer (100 mM, pH 7.0) were mixed in a RVA canister. The impact of proteins on RVA viscosity was studied by including the reducing agent DTT (0.15%) in the buffer. The temperature profile (31 min) included a temperature holding step (1 min at 50 °C), a linear temperature increase to 95 °C at 7.5 °C/min, a holding step (8 min at 95 °C), a linear temperature decrease to 50 °C at 7.5 °C/min, and a final isothermal step at 50 °C (10 min). The paddle speed was 960 rpm for the first 7 s (homogenisation of the sample) and then 160 rpm. The following parameters (Batey, 2007) were determined: pasting temperature (°C), i.e. temperature at which the viscosity first rises above the baseline during the initial heating phase; peak viscosity (centi-Poise, cP), i.e. the maximum viscosity during the cycle and a measure for shear resistance of particles; and end viscosity (cP), i.e. the viscosity at the end of the run (31 min). The RVA runs were reproducible as verified by three individual measurements with standard deviations (expressed in %) of the pasting temperature, peak and end viscosities of 0.7%, 1.1% and 0.4% respectively.

2.7. Statistical analysis

Statistical analyses were conducted using the Statistical Analysis System software 9.2 (SAS Institute, Cary, NC, USA). Tukey's Studentised Range tests were carried out and determined (significance level $P < 0.05$).

3. Results and discussion

3.1. Relation between the composition, gelatinisation temperature, SDSEP levels of semolina and spaghetti, and pasta cooking quality

The starch and protein contents of the semolina and spaghetti samples ranged from 68.9% to 76.2%, and from 11.7% to 14.7%, respectively (Table 1). Spaghetti 1, 2 and 12 had the highest pro-

tein contents (13.8%, 13.7% and 14.1% respectively). The levels of damaged starch of the semolina samples (4.2–7.1%) were lower than those of the dry spaghetti (6.8–10.0%). During pasta production (mixing and extruding), starch granules are damaged due to mechanical stresses (Lintas & D'Appolonia, 1973; Vansteelandt & Delcour, 1998). The most striking difference between the raw material (semolina) and the produced spaghetti was the level of SDSEP. While, typically, 80–85% of total semolina proteins was SDS extractable, spaghetti had much lower corresponding values (between 31% and 56% of total proteins). The results indicate that proteins became less extractable in the SDS medium, and presumably more polymerised, during pasta processing. There was also a striking difference between the level of SDSEP within the spaghetti (between 31% and 56%), and especially between spaghetti 1, 2 (55.8% and 55.0% respectively) and 15, 16 (32.3% and 31.2% respectively). In all likelihood, the differences in SDSEP contents between the spaghetti are related to differences in processing conditions. Lower levels of SDSEP may be attributed to more protein polymerisation (Lagrain et al., 2005) in the dry product caused by elevated drying temperatures (Lamacchia et al., 2007; Zweifel et al., 2003). Spaghetti 1 and 2 were most likely dried under gentle conditions, while spaghetti 15 and 16 were presumably dried under severe conditions. The other spaghetti were presumably dried under mild conditions. These assumptions are supported by the fact that the increasing DSC peak gelatinisation temperature went hand in hand with the decreasing content of SDSEP ($R^2 = 0.84$) as presented in Table 1. Spaghetti 15 and 16 indeed showed the highest peak gelatinisation temperatures. Drying of pasta under severe conditions induces a loss of order of starch during the beginning of the drying cycle followed by an increase of polymer order during the high temperature phase (Zweifel, Conde-Petit, & Escher, 2000), which leads to an increase of starch gelatinisation temperature (Cunin, Handschin, Walther, & Escher, 1995; D'Egidio, Mariani, Nardi, & Novaro, 1993; Yue, Rayas-Duarte, & Elias, 1999). In addition, using a pilot-scale process, Petitot et al. (2009) showed that 70% of the proteins of pastas dried at low temperatures (55 °C) was extractable in 1.0% (w/v) SDS, while 28% SDSEP was obtained when drying at very high temperatures (90 °C). From these results, it is tempting to deduce that spaghetti 1 and 2, with relatively

Fig. 1. The effect of different concentrations of dithiothreitol (DTT) on spaghetti SDS extractable protein (EP) levels before (A) and after (B) cooking.

higher SDSEP levels, were probably dried under gentle conditions, while spaghetti 15 and 16, with relatively lower SDSEP levels, were most likely dried under severe conditions.

To determine the differences in protein network formation of the spaghetti, the levels of SDSEP were compared for the semolina samples, dry (uncooked), and cooked spaghetti (Table 1). Ca. 80–

Table 1
Partial composition (% dm) and gelatinisation temperature of semolina samples and spaghetti.

	Starch (%)	Tp ^A (°C)	Damaged starch (%)	Proteins (%)		
				Total	SDSEP ^B in dry product	SDSEP ^B in cooked product
Semolina 1	75.2a	60.6fg	6.9def	13.5efg	84.8a	–
Semolina 2	74.1a	59.8h	5.6fg	14.4b	84.2a	–
Semolina 3	71.1a	61.4cdef	6.4ef	14.7a	79.9a	–
Semolina 4	68.9a	60.9defg	4.2g	14.2b	79.6a	–
Semolina 5	75.2a	60.1gh	7.1def	13.3fg	79.1a	–
Spaghetti 1	75.7a	60.2gh	6.8def	13.8cd	55.8b	16.8e
Spaghetti 2	73.5a	60.4gh	6.8def	13.7de	51.0b	14.9g
Spaghetti 3	71.4a	60.7efg	7.7bcdef	12.8ijk	46.2cd	20.8a
Spaghetti 4	76.2a	61.4cd	9.7ab	12.5k	43.0de	16.6e
Spaghetti 5	69.1a	61.0defg	8.7abcd	12.7jk	42.7de	20.3b
Spaghetti 6	74.7a	61.4cde	7.6bcdef	13.5ef	42.5de	19.5c
Spaghetti 7	73.6a	61.3cdef	8.5abcde	13.0hij	40.6ef	16.9e
Spaghetti 8	74.1a	61.9c	8.3abcde	13.7de	40.6ef	20.8a
Spaghetti 9	71.7a	62.0bc	8.4abcde	12.6k	40.3ef	15.5f
Spaghetti 10	75.5a	61.8c	10.0a	13.1ghi	40.2efg	12.4i
Spaghetti 11	72.0a	62.0bc	8.1abcde	13.8cd	39.4efg	15.9f
Spaghetti 12	74.7a	62.6ab	7.1cdef	14.1bc	36.9fgh	17.7d
Spaghetti 13	75.8a	61.8c	9.9abc	11.7l	36.5fghi	18.0d
Spaghetti 14	70.3a	61.7c	6.8def	13.5def	34.9ghi	14.0h
Spaghetti 15	73.4a	62.8a	9.7ab	13.2fgh	32.3hi	20.5ab
Spaghetti 16	71.7a	62.7ab	8.7abcd	12.8ijk	31.2i	14.4h

Values with the same letter within the same column are not significantly different ($P < 0.05$).

^A Tp: gelatinisation temperature.

^B SDSEP: sodium dodecyl sulphate extractable protein.

85% of total semolina proteins was extractable in the SDS containing medium. As a result of pasta drying, proteins became less extractable, and, most likely, more polymerised. This was most pronounced for spaghetti 15 and 16. Variations in the SDSEP levels after cooking of the spaghetti were less pronounced (12.4–20.8%). This indicates that protein polymerisation of spaghetti 1 and 2 occurred mostly during cooking, whereas, significant polymerisation had already occurred by the end of the drying process of the other spaghetti, and especially of spaghetti 15 and 16. As a result, the protein networks of spaghetti 1, 2 and 15, 16 were significantly different from each other. In the following text, a more in-depth comparison of these four samples is given.

Addition of increasing concentrations of DTT (0%, 0.01%, 0.1%, 0.5% and 1.0% w/v) to the SDS containing buffer used for extraction of dry (uncooked) spaghetti 1, led to more extractable protein (Fig. 1A). For spaghetti 16, much more DTT had to be added to the medium to extract the same levels of protein than for spaghetti 1. Thus, it seems that the rate at which proteins of uncooked (dry) spaghetti 16 became more extractable is slower than that of spaghetti 1. When the SE-HPLC profiles of extracts of dry (uncooked) and cooked spaghetti 1 and 16 (Fig. 2) with increasing concentrations of DTT were compared with the profile of durum wheat semolina extract as control, in the profiles of all samples with 0% DTT (Fig. 2), the first peak (retention time of 5.8 min) contained glutenin aggregates of very high molecular weight, while the second peak (retention time of 9 min) consisted of gliadin. The area in be-

tween represented glutenin of low molecular weight (Schofield, Bottomley, Timms, & Booth, 1983). Increasing concentrations of DTT depolymerised the high molecular weight protein material leading to enrichment of the gliadin peak in low molecular weight glutenin subunits. These profiles indicate that the proteins of spaghetti 16 polymerised more during processing, because high DTT concentrations were necessary to increase the protein extractability. In contrast, the profiles for unprocessed semolina and uncooked spaghetti 1 were quite similar. However, for spaghetti 1 still much more DTT was needed to obtain the same levels of SDSEP as for the unprocessed semolina. In addition, the profiles of spaghetti 16 before and after cooking were similar (Figs. 1B and 2), which showed that the spaghetti sample did not undergo much additional polymerisation during cooking. This was in contrast to what could be observed in the profiles of spaghetti 1 (Figs. 1B and 2). Evidently, protein polymerisation in spaghetti 1 but also in spaghetti 2, which showed comparable behaviour, occurred mostly during cooking. In the other samples, significant polymerisation had already occurred during processing. In conclusion, dry spaghetti 1 and 2 had low levels of polymerised protein (ca. 50% SDSEP in contrast to ca. 80% SDSEP in semolina), whereas dry spaghetti 15 and 16 had high levels of polymerised protein (ca. 30% SDSEP) and, hence, were dried under more severe conditions.

Pasta quality (Table 2) is expressed in terms of water absorption, leached material during cooking, and the texture properties firmness and stickiness. The texture of cooked pasta is generally

Fig. 2. SE-HPLC profiles indicating the effect of different concentrations of dithiothreitol (DTT) on the SDSEP levels of spaghetti 1 and 16 before and after cooking. Semolina served as control. The peak of purified gliadin [received from 70% ethanol (v/v) extraction of commercial gluten] dissolved in 2.0% (w/v) SDS sodium phosphate buffer (50 mM, pH 6.8) eluted at 9 min (result not shown).

recognised as its most important quality aspect. A high cooking quality can be defined as the result of high water absorption, low cooking losses, and good texture (high firmness and low stickiness). Spaghettis 1 and 2 had the highest cooking quality, while spaghettis 15 and 16 had the lowest quality among all spaghettis. In general, it has been reported that HT drying improves cooking properties, as revealed by lower cooking losses, increased firmness and lower surface stickiness (Resmini & Pagani, 1983; Zweifel et al., 2003). According to Zweifel et al. (2003) and Lamacchia et al. (2007), HT drying at low moisture conditions, during the late stage of the drying process, polymerises proteins into a protein network which entraps the starch granules. This network may restrict water absorption, thus preventing starch leaching and therefore decreasing stickiness. In this study, spaghettis 1 and 2 indeed absorbed more water during cooking than did the samples 15 and 16 (Table 2). However, spaghettis 15 and 16, dried under severe conditions, showed higher cooking losses and stickiness values than spaghettis 1 and 2, dried under gentle conditions (Table 2).

Table 2
Pasta cooking quality related data of 16 commercial spaghettis.

	Water absorption (g/g dm)	Leached material during cooking (%)	Firmness (N/mm)	Stickiness (mN/mm)
Spaghetti 1	2.01	4.4	7.2bcd	0.2h
Spaghetti 2	2.04	4.6	6.8def	4.2h
Spaghetti 3	2.13	5.7	6.4fg	46.3cde
Spaghetti 4	2.00	4.7	6.1gh	119.9a
Spaghetti 5	2.02	5.0	7.1bcd	60.1bc
Spaghetti 6	1.88	4.9	6.5efg	8.9gh
Spaghetti 7	1.88	5.0	6.6def	27.8efg
Spaghetti 8	2.12	5.7	7.1cd	71.6b
Spaghetti 9	1.94	4.6	7.4abc	16.2fgh
Spaghetti 10	2.05	3.9	6.5fg	55.4bcd
Spaghetti 11	1.97	5.3	6.9def	13.6fgh
Spaghetti 12	1.93	6.1	5.8bcd	11.5gh
Spaghetti 13	2.13	5.9	7.6ab	14.0fgh
Spaghetti 14	1.83	5.0	7.0cde	34.6def
Spaghetti 15	1.84	5.4	7.8a	104.2a
Spaghetti 16	1.92	5.9	6.6def	9.3gh

Values with the same letter within the same column are not significantly different ($P < 0.05$).

Table 3
The effect of dithiothreitol (DTT, 0.15%) on swelling power (SP, g/g) and carbohydrate leaching (%) during cooking of semolina and milled dry spaghetti samples.

	SP (g/g)			Carbohydrate leaching (%)		
	Control	+DTT	Difference	Control	+DTT	Difference
Semolina 1	16.6a	21.1ab	4.5	22.2b	21.4h	0.8
Semolina 2	15.6abcd	20.5abc	4.9	22.1b	21.8gh	0.3
Semolina 3	16.4ab	21.7a	5.3	22.6b	23.6fgh	−1.0
Semolina 4	13.6d	16.1d	2.5	22.3b	21.4h	0.9
Semolina 5	16.6a	20.9ab	4.3	22.4b	22.3gh	0.1
Spaghetti 1	14.3bcd	17.2d	2.9	26.6ab	26.1defgh	0.5
Spaghetti 2	14.2cd	16.6d	2.4	28.0a	24.4fgh	3.6
Spaghetti 3	15.4abcd	16.1d	0.7	33.1a	28.6abcde	4.5
Spaghetti 4	14.2cd	16.6d	2.4	28.3ab	28.4abcde	−0.1
Spaghetti 5	14.1cd	17.1d	3.0	29.4ab	30.3abc	−0.9
Spaghetti 6	15.4abcd	17.1bcd	1.7	30.6a	31.8ab	−1.2
Spaghetti 7	13.9d	16.7d	2.8	28.7ab	29.4abcd	−0.7
Spaghetti 8	14.7abcd	18.2bcd	3.5	29.9ab	31.8ab	−1.9
Spaghetti 9	14.6abcd	16.6d	2.0	28.4ab	27.7bcdef	0.7
Spaghetti 10	15.2abcd	16.5d	1.3	34.4a	30.5abc	3.9
Spaghetti 11	14.8abcd	16.4d	1.6	29.0ab	26.4cdefg	2.6
Spaghetti 12	15.3abcd	17.0d	1.7	28.6ab	28.6abcde	0
Spaghetti 13	16.1abc	18.2bcd	2.1	32.1a	30.4abc	1.7
Spaghetti 14	14.1cd	18.1bcd	4.0	28.2ab	33.1a	−4.9
Spaghetti 15	15.2abc	16.6cd	1.4	29.9ab	24.5cdefgh	5.4
Spaghetti 16	15.7abcd	16.6d	0.9	31.5ab	23.3efgh	8.2

Means with the same letter within the same column are not significantly different ($P < 0.05$).

In contrast to findings in literature (e.g. Cubadda et al., 2007; Dexter et al., 1981, 1983; Grant et al., 1993; Lamacchia et al., 2007; Novaro, D'Egidio, Mariani, & Nardi, 1993; Zweifel et al., 2003), results from this study indicate that spaghettis 1 and 2, with low levels of polymerised protein and presumably dried under gentle conditions, had the highest cooking quality as revealed by a combination of lower cooking losses, higher firmness and lower surface stickiness than the other spaghetti samples.

3.2. Swelling properties in relation to pasta cooking quality

3.2.1. General

It is evident that protein polymerisation occurs both during pasta production and the subsequent cooking step. Also, proteins, polymerised to a variable degree, hinder starch swelling during pasta cooking. Thus, next to protein polymerisation, also starch swelling properties must be evaluated and related to the cooking quality. In addition, the impact of proteins on the swelling properties was determined using the reducing agent DTT.

3.2.2. Swelling properties in the absence of shear stress

The milled spaghettis 15 and 16 had higher SP (respectively 15.2 and 15.7 g/g) and carbohydrate leaching (respectively 29.9% and 31.5%) during cooking than spaghettis 1 and 2 (SP 14.3 and 14.2 g/g, and carbohydrate leaching 26.6% and 28.0% respectively) as presented in Table 3. The higher the SP, the more the pasta particles can swell, and the more the carbohydrates leach into the cooking water. Interestingly, the spaghettis of highest cooking quality (spaghettis 1 and 2) showed less swelling and carbohydrate leaching than the spaghettis of lower cooking quality (Table 3).

The use of DTT (0.15% w/v) increased the SP for all spaghettis (Table 3). Increasing the concentration of DTT had no additional effect on SP and leaching behaviour for any of the milled spaghettis. The effect of DTT on SP was more pronounced for spaghettis 1 and 2 than for spaghettis 15 and 16.

3.2.3. Swelling properties in the presence of shear stress

Table 4 lists the pasting temperatures, peak and end viscosities of milled dry spaghetti samples. Milled spaghettis 1 and 2 had higher RVA peak and end viscosities than did the ground spaghettis

Table 4

The effect of dithiothreitol (DTT, 0.15%) on RVA pasting properties of semolina and milled dry spaghettis (12.0% w/v).

	Pasting temperature (°C)			Peak viscosity (cP)			End viscosity (cP)		
	Control	+DTT	Difference	Control	+DTT	Difference	Control	+DTT	Difference
Semolina 1	81.3	82.0	−0.7	3980	3755	225	4610	3890	720
Semolina 2	81.3	80.1	1.2	4270	3950	320	5340	4215	1125
Semolina 3	82.0	81.9	0.1	4605	4150	455	4735	3805	930
Semolina 4	82.9	81.9	1.0	5425	4830	595	5385	4415	970
Semolina 5	80.5	81.1	−0.6	4520	4075	445	5125	4145	980
Spaghetti 1	65.5	64.0	1.5	4615	3110	1505	4925	3665	1260
Spaghetti 2	66.5	66.0	0.5	4775	2545	2230	5365	3185	2180
Spaghetti 3	65.0	64.6	0.5	4750	2140	2610	5185	2945	2240
Spaghetti 4	67.2	66.0	1.2	3260	2205	1055	4460	2860	1600
Spaghetti 5	65.0	66.1	−1.1	4645	2190	2455	5045	2665	2380
Spaghetti 6	76.9	65.0	11.9	3565	4146	−581	4030	3845	185
Spaghetti 7	67.2	63.6	3.7	3545	3701	−156	4330	3798	532
Spaghetti 8	68.7	64.9	3.8	2720	2830	−110	3660	3259	401
Spaghetti 9	67.0	66.0	1.0	4415	2815	1600	5005	3210	1795
Spaghetti 10	68.9	66.0	2.9	3210	2565	645	4495	3180	1315
Spaghetti 11	69.0	65.9	3.1	3210	2605	605	4225	3035	1190
Spaghetti 12	79.4	66.5	12.9	3510	3355	155	4374	3515	859
Spaghetti 13	67.5	67.0	0.5	3710	2345	1365	4770	2835	1935
Spaghetti 14	66.7	64.6	5.1	3860	3470	390	4600	3480	1120
Spaghetti 15	78.9	66.9	12.0	3475	3555	−80	4735	3657	1078
Spaghetti 16	76.8	67.0	9.8	3615	2795	820	4780	3235	1545

15 and 16. This means that spaghettis 1 and 2 must have rigid particles, which during swelling, resisted shear during the heating process before disintegrating. No correlation was found between the SP and the RVA peak viscosity. In addition, the high peak viscosity may also be related to the low content of starch damage. Damaged starch can absorb more water at room temperature and hence swells earlier than native starch (Karkalas, Tester, & Morrison, 1992), which leads to lower peak viscosity and a lower pasting temperature (Güler, Köksel, & Ng, 2002). Spaghettis 15 and 16 had the highest pasting temperatures, which means that the swelling of the starch containing particles was postponed, probably due to the more aggregated proteins during processing of these pastas (Table 4).

Addition of DTT decreased RVA pasting temperatures and viscosities for almost all samples. This means that a disulfide linked protein network exists and increases the particles' shear resistance. The effect of DTT on the shear resistance of particles was more pronounced for spaghettis 1 and 2. The effect of DTT on the pasting temperature was more pronounced for spaghettis 15 and 16 which in these cases may be attributed to the postponed particle swelling due to the existence of a protein network. It is remarkable that the peak viscosities and the SP of the spaghettis 1, 2 and 15, 16 in the presence of DTT were quite similar (Table 3 and 4). This means that the starch properties of the starting raw materials for the commercial spaghettis are presumably similar. Thus, the different behaviour of the milled particles in TRIS–HCl buffer, as mentioned above, is mainly determined by the differences in protein properties.

The results indicate that, during cooking, the milled spaghettis 1 and 2 (the highest quality pastas) swell little and have the most shear resistant particles due to the protection by a protein network which, to a considerable degree, is formed during the cooking process itself. The SDSEP data and the gelatinisation temperatures of the dried pastas indicated that spaghettis 1 and 2 had been dried under gentle conditions. So, the protein network during cooking of the highest quality pastas (dried under gentle conditions) gives the particles more shear resistance than the network of the lowest quality spaghettis (dried under severe conditions) as the latter network lacked resilience. Addition of DTT during RVA analysis resulted in a protein network that no longer prevented the swelling of starch.

4. Conclusion

The results of this study indicate that a disulfide linked protein network exists in all spaghettis which provides shear resistance to particles and restricts starch swelling and subsequent leaching. An optimum in protein polymerisation during processing and/or cooking of spaghetti is critical for obtaining high quality pasta. When the proteins are polymerised too strongly during processing (in particularly during harsh drying conditions), they lack resilience to cope with starch swelling during cooking. This, in turn, results in more cooking losses and stickier spaghetti. This means that, in our view, too much protein polymerisation during processing is deleterious for spaghetti cooking quality. On the other hand, when the proteins are polymerised less during processing (in particularly during gentle drying), the polymerisation occurs mostly during cooking, and the proteins are more apt to follow the starch swelling resulting in higher quality pasta (less cooking losses and less sticky pasta). In conclusion, protein polymerisation is necessary during industrial drying to achieve high quality pasta, but the proteins must maintain enough resilience to cope with starch swelling during cooking. If not, the protein network cannot withstand the starch swelling, and, as a consequence, the final cooked pasta is stickier and more material is lost during cooking.

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