

Fractionation and Reconstitution Experiments Provide Insight into the Role of Starch Gelatinization and Pasting Properties in Pasta Quality

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Commercial durum wheat semolina was fractionated into protein, starch, water-extractable, and sludge fractions. The starch fraction was hydroxypropylated, annealed, or cross-linked to change its gelatinization and pasting properties. Spaghettis were made by reconstitution of the fractions, and their quality was assessed. Hydroxypropylated starches were detrimental for cooked pasta quality. Cross-linked starches made the reconstituted pasta firmer and even brittle when the degree of cross-linking was too high. These results indicate that starch properties play a role in pasta quality, although the gluten remains very important as an ultrastructure agent. It was concluded that, given a certain gluten ultrastructure, starch water uptake and gel properties and/or its interference with or breakdown of the continuous gluten network during cooking determine pasta quality.

Keywords: *Reconstitution; hydroxypropylated starch; cross-linked starch; pasta quality*

INTRODUCTION

In the preceding paper in this issue (Delcour et al., 2000), fractionation and reconstitution experiments provided insight into the role of gluten and starch interactions in pasta quality. Reconstituted samples had a higher quality than pasta made from semolina. This was not due to gluten aggregation during the fractionation process. Starches with changed surface characteristics did not influence the interaction behavior, indicating that starch–gluten interaction in raw pasta is mainly due to physical inclusion. All reconstituted pasta samples had generally the same cooking quality. It was concluded that the small changes in starch gelatinization behavior, caused by changed surface characteristics and manipulated granule size distributions, are of little importance for pasta quality.

According to Dalbon et al. (1981) and Resmini and Pagani (1983), during cooking of low-temperature (<60 °C) dried pasta, both gluten heat denaturation and starch gelatinization contribute to pasta quality. In the interspaces between starch granules, protein coagulation and interaction lead to the formation of a continuous and strengthened network which traps the starch, while the latter, by swelling and gelatinizing, occludes these interspaces. Therefore, the faster the starch swells and its spherulites disperse during pasta cooking, the slower the protein–protein interaction and the weaker the protein network in the resulting pasta. When the interaction of the coagulating protein with itself is more rapid than the starch swelling and gelatinization, and

the protein network is strong and elastic enough to prevent breakages, the cooked pasta will be firm. This hypothesis thus emphasizes the importance of starch gelatinization properties (gelatinization temperature and swelling and hence its interference with the continuous gluten network) for the quality of conventional dried pasta. In high-temperature dried pasta (Delcour et al., 2000, and references therein), proteins can already be coagulated into a continuous network that renders the starch granules less extractable and restricts their gelatinization and swelling during cooking. The quality of the cooked pasta is then correlated with the quality of this network.

Dalbon et al. (1985) prepared reconstituted pasta by mixing gluten with durum wheat starches that were dried with different drying profiles. Starches dried at low (ca. 55 °C) temperature produced the worst spaghetti; starches that were exposed to high temperatures (ca. 95 °C) at low humidity (ca. 13%) yielded reconstituted pasta of increased quality. These results suggest that those starch properties that can be changed by a heat–moisture treatment (Eerlingen et al., 1996, 1997) play a role in pasta quality.

Despite the above, no universal hypothesis on the role of starch in pasta exists. It was the aim of the present study to gain more insight in this area. As it was shown in the preceding paper in this issue (cf. supra) that small changes in starch gelatinization behavior were of little importance for pasta quality, we here used reconstitution experiments in which the starch fraction was changed more drastically. The starch gelatinization temperature was substantially increased by an annealing procedure (Jacobs et al., 1995) and decreased by means of chemical modification (hydroxypropylation) to evaluate the role of the starch gelatinization temperature (Frey, 1970) in pasta quality. As Frey (1970), Dexter and Matsuo (1979a), and D'Égidio et al. (1983)

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pointed to the importance of amylose and pasting behavior in pasta-making, we also decided to perform reconstitution experiments with a series of increasingly cross-linked starches.

MATERIALS AND METHODS

Durum wheat semolina was obtained from N.V. Soubry (Roeselare, Belgium). All used reagents were at least of analytical grade.

Semolina Fractionation and Characterization. The semolina was fractionated into starch, protein, sludge, and water-extractable fractions. The process used and the fractions obtained have all been described previously by Delcour et al. (2000).

Starch Modifications. Starch Annealing. A two-step annealing procedure was used. The starch fraction was suspended in water (1:2, w/w), and the suspension was heated for 24 h in a sealed container in a water bath at a constant temperature. The annealing temperature was chosen as a function of the gelatinization temperature of the native starch, i.e., 3.3% below the gelatinization peak temperature (K) as determined by differential scanning calorimetry (DSC) (cf. *infra*). After a 24 h incubation period, the suspension was Buchner-filtered and the residue was dried overnight at room temperature. The resulting starch was referred to as one-step-annealed starch. Two-step-annealed starch was prepared by incubating the starch suspensions, after first period of 24 h at the first annealing temperature and another 24 h at a higher temperature, 3.3% below the gelatinization peak temperature (K) of the one-step-annealed starch. After this 48 h of incubation, the two-step-annealed starch was Buchner-filtered, washed with ethanol, and dried in the same way as the one-step-annealed starch. It is further referred to as AN.

Starch Hydroxypropylation (Wootton and Manatsathit, 1984). Starch (600 g) was suspended in a solution prepared by adding 7.8 g of NaOH and 90 g of Na₂SO₄ in 720 mL of demineralized water. Suspensions were placed in stoppered bottles with magnetic stirrers in a water bath at 38 °C. Propylene oxide (18 or 36 mL) was added, and the starches were incubated for 24 h under continuous stirring. After that, the starches were filtered on a Buchner filter, washed with water until the wash water was sulfate-free (as detected with 1 M BaCl₂), and air-dried. They are further referred to as etherified starches E18 and E36, respectively.

Starch Cross-Linking (Cooreman et al., 1995). Starch (1500 g) was suspended in 3500 mL of 0.107 M NaOH and 38, 114, 228, or 1140 mL of a 5.0% sodium trimetaphosphate solution was added. This suspension was incubated for 18 h in a water bath at 40 °C under continuous stirring. After incubation, the suspension was neutralized to pH 6.5 with 6.0 M HCl. Cross-linked starches were filtered on a Buchner filter, washed three times with water (1500 mL), and air-dried. They are further referred to as CL38, CL114, CL228, and CL1140, respectively.

Starch Characterization. DSC and rapid visco analysis (RVA) were as described before (Delcour et al., 2000).

Reconstitution, Pasta Production, and Quality Evaluation. Pasta samples were reconstituted as described earlier (Delcour et al., 2000) with the original yield of each fraction as a basis. Pasta was produced at least in duplicate and dried as already described (Delcour et al., 2000). In what follows reconstituted samples can be recognized by the abbreviation "Re" in the sample codes. The drying temperature never exceeded 70 °C. Pasta quality assessment comprised color analysis, evaluation of the surface condition and the viscoelastic index (VI) of the cooked pasta, and determination of water absorption and losses during cooking (Delcour et al., 2000). All quality determinations (and pasta cooking experiments) were performed at least in duplicate on each produced sample. The results are reported as averages of the analytical data obtained, with the corresponding pooled standard deviations (Delcour et al., 2000).

Table 1. Average Gelatinization Onset (T_0), Peak (T_p), and Conclusion (T_c) Temperatures, Gelatinization Intervals ($T_c - T_0$), Gelatinization Enthalpies (ΔH^f), and Enthalpies of the Melting of Amylose-Lipid Complexes (ΔH^s) of the Native and Modified Starches As Measured in DSC^a

sample ^b	T_0 (°C)	T_p (°C)	T_c (°C)	$T_c - T_0$ (°C)	ΔH^f (J/g)
SF	50.2 (0.5)	58.5 (0.3)	65.9 (0.5)	15.7	12.2 (1.6)
AN	62.3 (0.2)	65.3 (0.2)	68.5 (0.3)	6.2	9.7 (0.8)
E18	46.3 (0.6)	53.6 (0.4)	58.0 (0.4)	11.7	5.4 (2.0)
E36	42.3 (0.0)	49.7 (0.2)	53.7 (0.1)	11.4	4.7 (0.8)
CL38	54.6 (0.0)	59.2 (0.1)	63.1 (0.2)	8.5	9.2 (0.8)
CL114	54.7 (0.4)	59.2 (0.3)	63.3 (0.3)	8.6	9.5 (1.6)
CL228	54.4 (0.1)	59.0 (0.1)	62.7 (0.0)	8.3	8.3 (0.1)
CL1140	52.9 (0.3)	58.7 (0.2)	63.4 (0.1)	10.5	11.4 (1.8)

^a Averages of at least triplicate measurements, with standard deviations in parentheses. ^b Abbreviations used: SF = starch fraction; AN = annealed starch; E = etherified starch; CL = cross-linked starch.

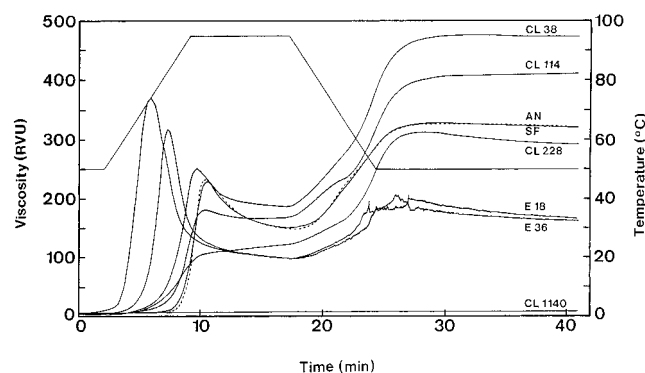


Figure 1. RVA viscosograms of the starches made at a concentration of 9.9%. For sample codes, see the text.

RESULTS AND DISCUSSION

Starch Characterization. The gelatinization enthalpies (ΔH^f) and the DSC gelatinization transition temperatures (T_0 , T_p , and T_c) of SF and the modified starches are represented in Table 1. RVA viscosograms (Delcour et al., 2000) of these starches are represented in Figure 1.

Annealed and Hydroxypropylated Starches. The two-step annealing procedure led, as expected (Jacobs et al., 1995), to an increase of the gelatinization temperature. Also expected was the narrower gelatinization range. Hydroxypropylation decreased the starch gelatinization enthalpy (ΔH^f) and decreased the peak gelatinization temperature by about 5 and 9 °C for E18 and E36, respectively (see Table 1). It seems reasonable to assume that the effect is to a certain degree to be ascribed to the treatment conditions (presence of alkali in the reaction medium) rather than to the hydroxylation treatment itself. The observed effects concur with earlier reported studies on hydroxypropylated durum wheat (Nelson, 1982), field pea (Hoover et al., 1988), and maize (Wootton and Manatsathit, 1984) starches. The decrease in gelatinization temperatures was more pronounced for T_c than for T_p or T_0 , with T_0 being the least affected (Table 1). This contrasts with the observations by Hoover et al. (1988) and Wootton and Manatsathit (1984).

From Figure 1, it is also clear that hydroxypropylation influenced the pasting behavior of the starches. Results concur with those of Nelson (1982). The peak viscosity was observed at lower temperatures than for the control starch. Higher peak viscosities can be explained by higher granule swelling. The larger shear thinning,

Table 2. Description of the Samples, Average Color Scores, Minimal Cooking Times (*T*), Surface Conditions, Viscoelasticity Indices, Cooking Weights, and Cooking Losses^a

description of the sample ^b	color scores			<i>T</i> (s)	surface condition			viscoelasticity index				water absorption (%)	cooking loss (%)
	brown (100- <i>L</i>)	red (<i>a</i>)	yellow (<i>b</i>)		<i>T</i> + 6	<i>T</i> + 11	av	<i>T</i> + 1	<i>T</i> + 6	<i>T</i> + 11	av		
ReSF	40.2	2.2	31.1	454	7.3	6.9	7.1	13.0	9.6	6.0	9.5	299	8.8
				(27)	(0.4)	(0.6)		(0.8)	(0.7)	(0.5)		(3)	(0.2)
ReAN	43.1	1.6	28.4	443	6.6	4.8	5.7	12.9	8.7	5.0	8.9	285	9.6
				(29)	(0.4)	(0.4)		(0.8)	(0.6)	(0.8)		(0)	(0.1)
ReE18	40.6	2.2	30.2	412	6.3	3.7	4.5	8.6	5.9	4.0	6.2	316	8.5
				(15)	(0.8)	(0.5)		(0.3)	(0.3)	(0.3)		(4)	(0.4)
ReE36	42.2	1.9	29.1	368	4.0	1.5	2.3	6.3	3.9	1.2	3.8	306	8.9
				(15)	(0.0)	(0.6)		(0.7)	(0.4)	(0.8)		(7)	(0.8)
ReCL38	40.6	2.2	30.2	428	6.9	6.2	6.6	14.3	11.5	7.9	11.2	280	8.6
				(29)	(0.3)	(0.3)		(0.4)	(1.2)	(0.5)		(2)	(0.3)
ReCL114	40.6	2.1	30.7	428	7.1	6.6	6.8	16.1	12.6	8.1	12.3	274	8.3
				(15)	(0.5)	(0.6)		(0.7)	(0.4)	(0.7)		(1)	(0.1)
ReCL228	40.4	2.0	30.9	435	7.5	6.5	7.0	16.1	13.9	9.6	13.2	271	8.9
				(17)	(0.1)	(0.4)		(0.4)	(0.8)	(0.9)		(3)	(0.1)
ReCL1140	39.9	2.3	31.1	444	7.7	6.9	7.3	18.9	12.8	5.4	12.4	245	8.2
				(13)	(0.1)	(0.6)		(1.0)	(1.0)	(1.4)		(7)	(0.2)

^a Where relevant, pooled standard deviations are represented in parentheses. ^b Abbreviations used: Re = reconstituted pasta sample; SF = starch fraction; AN = annealed starch; E = etherified starch; CL = cross-linked starch.

observed for the hydroxypropylated starches, is due to faster disintegration of the greatly swollen, modified starches. Unexpectedly, no large differences in pasting behavior could be detected between the annealed and the native starches. Only the slightly higher DSC gelatinization temperature of the first is reflected in its pasting behavior.

Cross-Linked Starches. From the DSC data (Table 1) it is clear that cross-linked starches generally had the same gelatinization peak temperatures as SF. However, the gelatinization range was smaller. The most cross-linked starch (CL1140) showed a somewhat different DSC behavior. Although T_p was almost equal to that of the other cross-linked starches, the gelatinization range was clearly larger.

However, differences between the cross-linked starches became evident in the RVA (Figure 1). Using the theory of Steeneken (1989), the high viscosity of the CL38 sample could be explained by the higher rigidity of the swollen starch. With increased cross-linking, granules swelled less and the viscosity was governed by the degree of swelling and solubility of the starch. A higher degree of cross-linking with consecutive lower swelling and starch solubilization then led to lower viscosities for CL114 and CL228. The CL1140 was so severely cross-linked that no viscosity increase during the temperature–time profile appeared, indicating that this starch hardly swelled and barely released any amylose during gelatinization. In conclusion, the CL samples formed a series of mildly to very severely cross-linked starches with gradually less swelling and starch solubilization.

Pasta Properties. The dried pasta samples visually resembled industrial pasta commercially available in Belgium (“spaghetti fijn extra”, Soubry, Roeselare, Belgium). All reconstituted (Re) samples had more or less the same color scores (Table 2) except for ReE36 and ReAN.

Furthermore, the increased susceptibility to gelatinization of hydroxypropylated starches (cf. supra) led to lower cooking times for ReE18 and ReE36 (Table 2). Cross-linking did not change the gelatinization temperature to a large extent (cf. supra). Concomitantly, only a limited and nonsignificant increase in cooking time with increasing degree of cross-linking was observed.

Increased degrees of cross-linking reduced the swelling and the simultaneous water absorption during cooking (Table 2).

Table 2 also lists the surface condition scores. Starch hydroxypropylation was very detrimental for the pasta surface condition. The surface became slimy after cooking. Annealing also decreased the surface quality of the obtained pasta product. In contrast, cross-linking improved its surface quality.

Hydroxypropylation not only deteriorated the pasta surface (cf. supra), but also the firmness of the cooked pasta (Table 2, VI scores). The samples swelled enormously during cooking and formed one bulky mass. Cross-linking on the other hand increased the pasta firmness (see the VI values at $T+1$ for the cross-linked starches, Table 2). However, once the degree of cross-linking was too high, samples were no longer elastic but became brittle when overcooked, explaining the lower values for ReCL1140 at $T+6$ and $T+11$.

When Nelson (1982) added up to 10% hydroxypropylated or cross-linked starch to durum flour, differences between the sample firmness were not significant, probably because of low incorporation levels and low degrees of modification.

Frey (1970) obtained a porridge after cooking pasta reconstituted from severely cross-linked starch, suggesting that gelatinization and pasting are necessary for cooking quality. Although in the present work the ReCL1140 pasta sample containing severely cross-linked starch was different (brittle) from the other CL pasta samples, a porridge was not at all obtained.

Water Absorption and Losses during Cooking. Cross-linking had a clear effect on water absorption (Table 2). With increasing degrees of cross-linking, the water absorption decreased. As annealing reduces the starch swelling power (Vansteelandt, 1995), the lower water absorption of ReAN could be explained in the same way. However, it is of note that the pasting behavior of AN resembled very much that of SF (cf. supra). In contrast to the above, hydroxypropylation caused starches to swell more and absorb more water during gelatinization, explaining the higher water absorption for the ReE18 and ReE36 samples. Furthermore, the lower water absorption of the ReE36 pasta than that of ReE18 is due to the shorter cooking time of the latter.

No logical trend in the cooking loss data (Table 2) could be found. Results are all in a rather narrow range (8.2–9.6%). Earlier investigations (Dexter and Matsuo, 1979b, and references therein) reported that cooking loss does not correlate well with other spaghetti quality parameters.

Stickiness after Cooking. Directly after being cooked, ReE samples were slimy and ReCL samples were mat. After a given time, ReE samples became really sticky. ReCL samples on the contrary became not sticky at all.

GENERAL DISCUSSION

Starch plays an important role in pasta quality. Indeed, by gradually modifying the starch fraction in reconstituted pasta, the quality also changed gradually.

The use of hydroxypropylated starches was detrimental for the pasta surface condition and the VI. Although cooking times decreased, these pastas absorbed more water and the cooked products were very sticky. Cross-linking gradually increased the cooking time because of lower swelling and water absorptions. The pasta surface condition was improved by use of cross-linked starch. A gradual increase of the degree of cross-linking of the starch also increased the VI of the corresponding pasta samples. However, once the starch was cross-linked so severely that no significant pasting behavior could be observed (Figure 1, sample ReCL1140), pasta samples became brittle during overcooking and had a low VI.

These results support the observation by Frey (1970) that differences in pasta consistency reflect the characteristics of concentrated gels, made by gelatinization of the respective starches in the absence of mechanical stress. In other words, starches that form firmer gels yield pasta with higher VI. In turn, these starch gel properties can be correlated with the starch swelling and water absorption capacity. Our results indicate that pasta with a higher water absorption (Table 2) and higher starch swelling (Figure 1) has a lower VI (and vice versa). Frey (1970) for reconstituted pasta samples (made from starches of the same botanical origin) also found a clear negative correlation between the pasta firmness and its water uptake.

Starch does not form a bulky gel in good-quality high-temperature dried pasta, but is more or less enmeshed in a (partial) gluten network. The quality of this network then correlates to the physical properties of the cooked pasta (cf. supra). It can be assumed that pasta quality is thus influenced by the interference with or the breakdown of the continuous gluten network by the gelatinizing, swelling starch. As the starch swells earlier and more intensively in the ReE samples, the protein structure is destroyed more and the pasta quality is impaired. In this view, the gradually lower swelling of the starch in the ReCL samples gradually causes a better conservation of the gluten network and a consequently better pasta quality after cooking. It can thus be concluded that the preservation of the gluten network during cooking is very important toward pasta quality. Starch may not swell too much, and the gluten network should be strong and elastic during cooking to prevent its destruction and to provide a good pasta cooking quality.

It is of note that the preceding paper in this issue (Delcour et al., 2000) concluded that the slight changes in starch gelatinization behavior that were caused by

starch modifications (lipid or protein removal/changed granule size distribution) were unimportant for pasta quality. In view of the above, it seems logical that these small changes were not important enough to make a difference in the preservation or destruction of the gluten network during cooking. Consequently, pasta quality was generally the same for all samples. The starch modifications in this work were more important with respect to the pasta's ability to destroy or interfere with the continuous gluten network during pasta cooking in a way that it loses its strength.

The above-mentioned hypotheses fit in with other observations in the literature. It seems logical that amylose and botanical origin (Dexter and Matsuo, 1979a), starch damage (D'Egidio et al., 1983), or heat–moisture treatment (Dalbon et al., 1985) is important for pasta quality. Indeed, each variation in starch properties that has an impact on its water uptake, gel consistency, and gluten breakdown capacity may influence pasta quality. In this line of thinking, our results for the ReCL samples are easier to understand than the previously mentioned observations by Frey (1970), who obtained a porridge after cooking pasta with severely cross-linked starch.

CONCLUSIONS

Our work indicates that starch properties are important for pasta quality. A hypothesis explaining pasta quality must grant a role not only to protein and pasta ultrastructure, but also to starch properties. Gluten as an ultrastructure-forming agent remains very important toward pasta quality. However, given a certain gluten ultrastructure, starch water uptake and gel properties and/or its gluten network breakdown ability during cooking become important in explaining pasta quality.

Taken together, the preceding paper in this issue (Delcour et al., 2000) in which slight changes in starch gelatinization behavior were shown to be unimportant for pasta quality and the present work allow the conclusion that modifications of starch have to be substantial if they are to affect the starch gel properties, to destroy the continuous gluten network during pasta cooking, and/or to have an appreciable impact on pasta quality.

ABBREVIATIONS USED

AN, annealed starch; AX, arabinoxylans; CL, cross-linked starch; ΔH^I , gelatinization enthalpy; ΔH^B , enthalpy of the melting of amylose–lipid complexes; DSC, differential scanning calorimetry; E, etherified starch; RVA, rapid visco analysis; RVU, rapid visco units; SC, surface condition; SF, starch fraction; 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.

ACKNOWLEDGMENT

Etn. Joseph Soubry N.V. (Roeselare, Belgium) is thanked for supplying the semolina, J. Ingelbrecht (this laboratory) for helpful discussions, and M. Sindic (Department of Agro-Industries, Agricultural State University, Gembloux, Belgium) for the use of the wheat fractionation equipment.

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Received for review August 31, 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).

JF991052E