Effect of iodine in semolina matrices

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List of Abbreviations: K/S, absorption/scattering coefficient; DP, degree of polymerization

Abstract: The effect of starch-protein interactions on the ability of linear starch chains to bind iodine was investigated in 4 types of semolina. Based on K/S (absorption/scattering coefficient) spectra, obtained after equilibration above K_2SO_4 and exposure to iodine vapor, and X-ray diffraction, semolina samples showed differences in chain mobility, iodine binding capacity and crystalline order. After removing protein from the samples, starch exhibited a higher iodine binding capacity, suggesting greater starch chain mobility, and low crystalline order. The results suggest that protein and/or starch-protein affect the packing arrangement of starch polymers within the granule.

Durum wheat (*Triticum turgidum* L. var. *durum*) is considered the most suitable raw material for pasta. Although up to 80% of dry matter in semolina is starch, this component has received limited research attention up-to-now. Even in the few studies that have focused on blends of starch and gluten or on starch and gluten isolated from raw materials (Delcour et al., 2000a; Delcour et al., 2000b; Yue et al., 1999; Vansteelandt and Delcour, 1998; Dalbon et al., 1985; Lintas and D'Appolonia, 1973; Sheu et al., 1967), the role of starch, per se and more specifically, of its interaction with other semolina components has not received much attention.

Recently, the ability of iodine to form complex with starch polymers in the native granular systems has been widely exploited for investigating the architecture of starches from different botanical origin including cereals [corn (*Zea mays* L.), high amylose corn, waxy corn, wheat (*T. aestivum* L.), rice (*Oryza sativa* L.), waxy rice], pulses [chickpea (*Cicer arietinum* L.), mung bean), and tubers [potato (*Solanum tuberosum* L.), waxy potato, tapioca (*Manihot esculent*a Crantz)] (Manion et al., 2011). Although there is some evidence that starch-protein interactions interfere with glucan polymer-iodine complex formation in a dilute solution (Liu et al., 2009), in a previous study it was demonstrated that the presence of components other than starch (such as proteins, lipids and non-starch polysaccharides) did not interfere with the formation of granular starch-iodine complex in gluten-free matrices (Marti et al., 2011). The objectives of the present research were to explore the possibility of investigating starch-protein interactions in a semolina matrix by using iodine vapor at low moisture contents.

In this study, semolina from two durum wheat cultivars (Latinur, with 14.9 % d.b. protein, 10.4 % d.b gluten, 1.1 % d.b. lipid, 71.7 % d.b. total carbohydrates; and PR22D40, with 14.2 % d.b. protein, 9.6 % d.b gluten, 1.1 % d.b. lipid, 71.5 % d.b. total carbohydrates;

CRA, Rome, Italy) and two semolina from commercial durum wheat blends (Semolina 1 with 14.3 % d.b. protein, 13.2 % d.b gluten, 1.1 % d.b. lipid, 69.5 % d.b. total carbohydrates; and Semolina 2 with 10.4 % db protein, 8.2 % db gluten, 0.8 % db lipid, 74.1 % db total carbohydrates, Molino Grassi, Parma, Italy) were used (60% between 400 and 250 μm and 40% less than 250 μm). These were chosen because of differences in the pasta-making performances (Alveographic W 165 $*10^{-4}$ J, 125 $*10^{-4}$ J, 198 $*10^{-4}$ J, and 154 $*10^{-4}$ J for Latinur, PR22D40, Semolina 1, and Semolina 2, respectively). Starch samples were isolated from semolina according to Park et al. (2006). The nitrogen content of all starches was less than 0.1% (Dumas combustion method; Leco EP 528, Leco Instruments Ltd Canada). Semolina samples and starch isolated from semolina were exposed to iodine vapour at 0.97 a_w as described by Saibene and Seetharaman (2006). Wide-angle X-ray diffraction measurements were carried out on samples after equilibration at 0.97 a_w, before and after iodine exposure (Rigaku Powder Diffractometer equipment - Rigaku Co., Tokyo, Japan), according to Marti et al. (2011). The K/S value of the samples after iodine exposure was measured at wavelength ranging from 400 to 700 nm, at 10 nm intervals, using a CM 3500-d Spectrophotometer (Konika Minolta, Mahwah, NJ, USA).

Absorption spectra of semolina samples after iodine exposure are shown in Figure 1. No distinct peaks are evident in any of the semolina samples following equilibration and exposure to iodine. However, Semolina 2 exhibited the highest absorption values, followed by Semolina 1, while no differences were detected between Latinur and PR22D40. The high K/S values for semolina 2 suggest the presence of higher amounts of mobile polymers capable of binding iodine. The iodine absorption corresponded to L* values; the higher the iodine absorption, the darker the color and higher the K/S values. The different chain mobility of semolina samples is likely related not only to the starch content (the higher the total carbohydrates, the higher the K/S) but also to the organisation of starch-protein polymers and their interactions. Another observation to be noted here is that the two varieties exhibit similar attributes where the commercial blends exhibit differences in K/S spectra.

When the proteins are removed from semolina, a general increase in iodine binding and mobility of polymer chains was detected, along with dual peak maxima and corresponding changes in luminosity values (Figure 1). Furthermore, as with semolina samples, greater differences were observed with the two commercial blends than in the two varieties. Starch from semolina 1 exhibited the highest K/S value, suggesting the presence of a high population of more mobile glucan polymers available to form inclusion complexes with iodine. The results suggest that the level of interaction with iodine in starch granule is affected not just by the presence of glucan polymers, but, especially by their ability to form single helices in the presence of iodine.

Furthermore, for all samples, dual peaks of absorption maxima were detected at 480 and 540 nm (Figure 1), corresponding to the mobility of chains with a DP of 12 and 36, respectively (Bailey and Whelan, 1961). The absence of K/S peak in semolina samples could be attributed to the presence of starch-protein interactions, responsible for a more tightly packed matrix compared to isolated starch. In fact, the starch-iodine complexation is more likely to occur in the less organized and more mobile amorphous regions, than in the crystalline regions (Saibene et al., 2008). The differences in absorption values between semolina and starch suggest that the removal of protein from the samples highlighted a different arrangement of the amorphous regions in the starch of different samples. While investigating the iodine binding properties of a ternary complex (starch, whey protein, free fatty acids) in a dilute system, Liu et al. (2009) demonstrated that the presence of whey protein at high concentration delayed the amylose-iodine reaction, while protein-starch interaction had no effect on the λ_{max} values. Thus, our preliminary study suggests that the presence of protein and their interaction with starch affect the formation of starch-iodine complex thereby changing the mobility and the unit chain of the polymer chains available to complex with iodine, since the K/S absorption value is dependent on chain mobility (Saibene and Seetharaman, 2006) and the λ_{max} is dependent of DP (Bailey and Whelan, 1961).

The X-ray diffractograms of semolina samples equilibrated above K_2SO_4 are shown in Figure 2. As expected, all the samples showed the A-type diffraction pattern with peaks at 15°, 17°, 18°, 20°, and 23° 2θ, typical of cereal. After sample iodination, the intensity of the main diffraction peaks (13°, 15°, 17°, and 18° 2θ decreased and the intensity of 20° 2θ peak increased suggesting increased single helical complexation with iodine. Moreover, a new peak at 7° 2θ also appeared in the samples suggesting a higher level of order among the single helical chains. The main changes observed in X-ray diffraction of starches following iodine exposure were an increase in the peak at 20° 2θ and new peak appearing at 5° 2θ (data not shown) as has been reported previously for other starches (Waduge et al., 2010). The interesting observation in this study is the significant impact on the fingerprint peaks in semolina following iodine exposure but not in the isolated starch samples. Thus the polymers complexing with iodine diminished the crystalline packing in starch when present with proteins, but not when exposed to iodine without the proteins. These observations would allow for a possible way to explore the role of starch-protein interactions in semolina functionality. The presence of protein, and likely of starch-protein interactions, affect the packing arrangement of starch polymers within the granule. Moreover, the iodine-binding technique highlighted differences in starch arrangement, both in amorphous and ordered regions, in semolina samples. Further studies are in progress to better understand how the differences in starch architecture between different semolina samples, and likely starch-protein interactions, can affect the starch arrangement in pasta and, consequently, its cooking behavior and textural properties.

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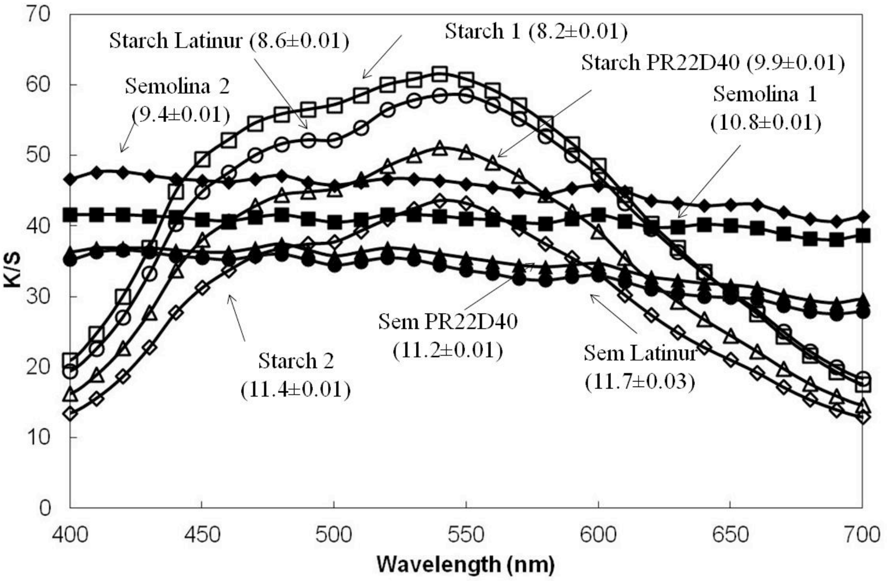

Figure 1. K/S value of semolina (closed symbol) and isolated starch (open symbol) of Latinur (circle), PR22D40 (triangle), blend 1 (square), and blend 2 (rhombus) samples exposed to iodine vapor following equilibration over K_2SO_4 saturated solution (0.97 a_w). Luminosity values in bracket.

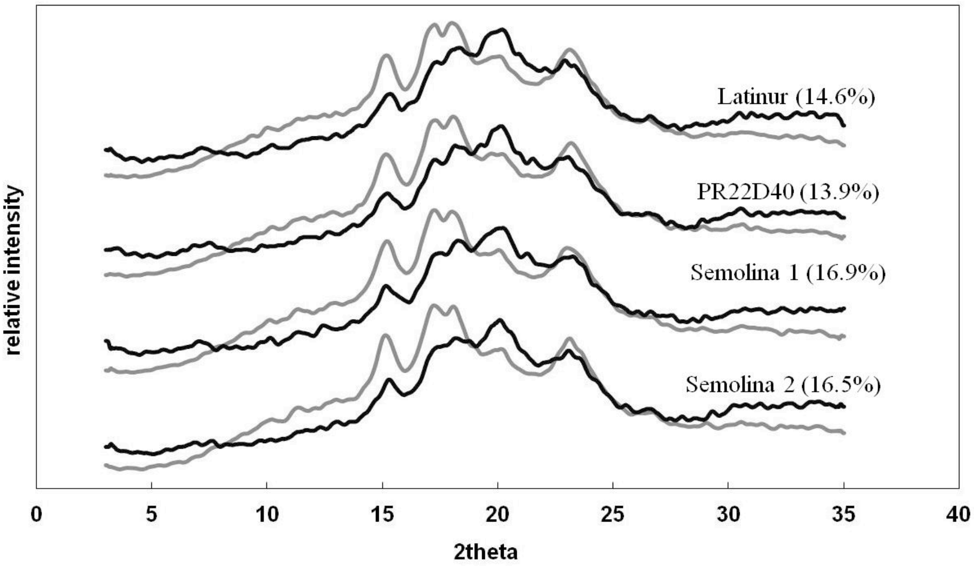

Figure 2. X-ray powder diffraction spectra of semolina samples following equilibration above K_2SO_4 (0.97 a_w). Light color represents the control sample, while dark color represents the iodine exposed sample. The graphs are offset for clarity. Moisture content in bracket.