Hydration Behavior of Starch Mixtures: Toward Rational Gluten-Free Bread Formulation

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Wheat is a staple in the human diet, providing about the 20% of food calories and proteins consumed worldwide. [1] Wheat flour commonly contains starch (70 – 75 %) and proteins (10 – 12 %), including gluten, in addition to water and other minor components. However, over the last decades, the increasing incidence of gluten sensitivity, gluten intolerance and celiac disease has raised global concern, reinforcing the perception of gluten-free products as healthier alternatives and consequently increasing consumer demand. Nonetheless, the production of gluten-free breads and bakery products remains a major challenge, as gluten-free doughs are generally less cohesive and elastic than conventional ones, resulting in breads with lower volume and poorer texture and taste. [2]

Current improvement strategies rely on specific additives that can mimic the viscoelastic properties of gluten, but the selection of starches still plays a dramatic role in the final properties of doughs. In fact, different starches show different water absorption capacity, making water addition a critical step in gluten-free food production. [2] It is well known that dough water content, as well as water absorption by individual ingredients, crucially influences bread quality, affecting its rheology, volume and texture. [3]

Mixtures of different starches have been used to improve bread properties and overall acceptability [2], but a comprehensive understanding of the role of each ingredient, especially during hydration, is still lacking. Our research aims at filling this gap, to rationalize and optimize gluten-free dough formulations, thus enabling larger-scale and more cost-effective production. The target product is gluten-free "pani carasau", a traditional flatbread from Sardinia, with long shelf-life and high nutritional value. [4]

In this work, the physicochemical properties of starch granules from three different cereals (*i.e.* deglutinated wheat, WS, rice, RS, and corn, CS) were systematically characterized. The structure and morphology of the starches at different lengthscales were investigated under different hydration conditions, revealing significant differences among the samples. Confocal Laser Scanning Microscopy (CLSM) images revealed striking differences in granule size and shape (Figure 1). Moreover, differences in the hydration behavior emerged when the granules were equilibrated at different Relative Humidity (RH = 0 – 100%).

The changes observed at the microscale could also be correlated with structural variations occurring at smaller lengthscales. In particular, characteristic domains in the 5 – 10 nm range, investigated by Small Angle X-ray Scattering, local order, associated to specific peaks in Fourier-Transform Infrared, FTIR, spectra, and overall crystallinity, determined by X-Ray Diffraction (XRD) were found to depend on both the starch type and water content.

Starch water content and free water index were quantified through Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) measurements. Notably, starch granules equilibrated at RH = 100% showed no detectable free water, suggesting that under these conditions the granules remain far from a fully-swollen state.

The latter condition occurs in formulations in which bound water has reached a maximum, while additional water contributed only to the free water fraction. In such conditions, the hydration behavior of each starch granule, even within mixtures, is expected to be independent of the other components.

The mechanical properties of starch dispersions in excess water were assessed through Mixolab® and rheological measurements. Mixolab® is an instrument specifically designed to evaluate dough behavior under continuous mixing, after water addition and during changes in temperature, including heating-induced starch

gelatinization and the subsequent cooling-induced retrogradation. The profiles of Torque VS Time confirmed the different hydration behavior of starches, and could be related to the rheological profiles of the mixtures. The interpretation of the rheological data was not trivial, as friction plays a critical role in concentrated starch dispersions [5], with granules’ size and shape drastically affecting the mechanical response.
Overall, our results contribute to a better understanding of the role of starch hydration within complex mixtures, paving the way toward the rational formulation and optimization of gluten-free products.

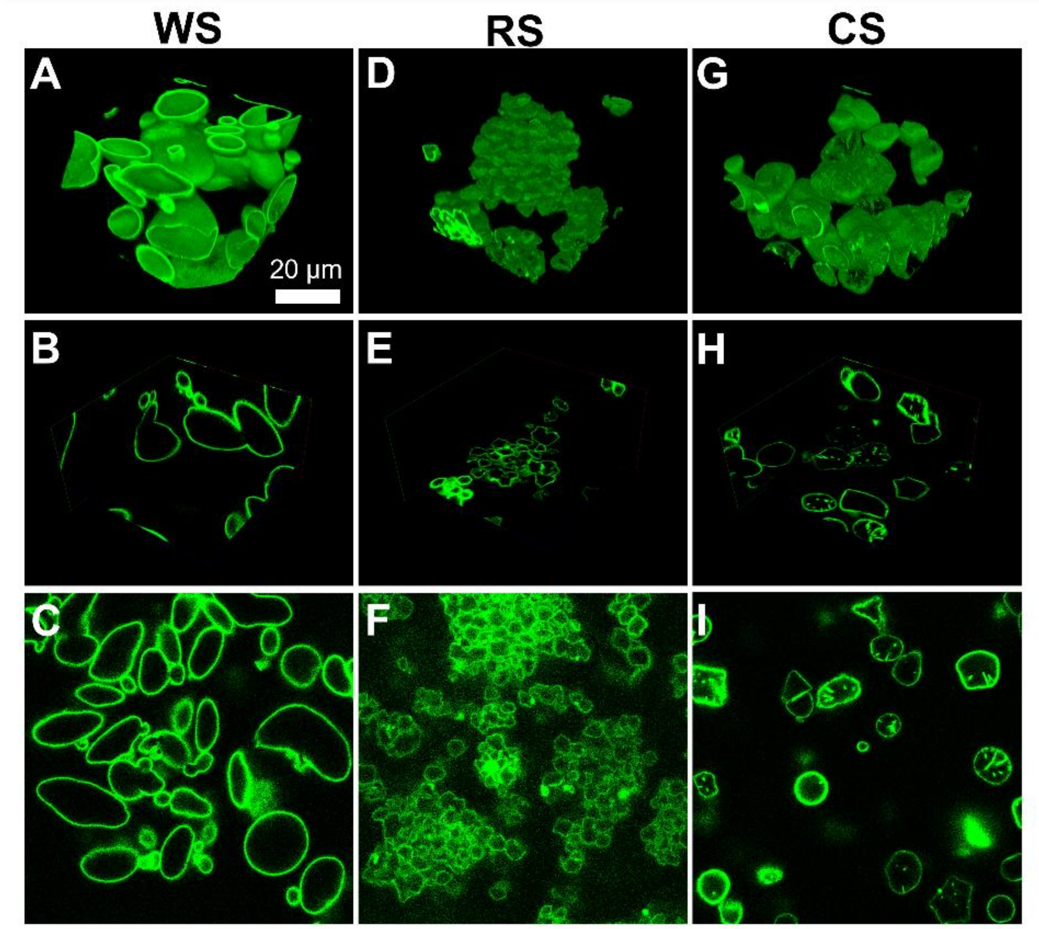

Figure 1 – CLSM images of Wheat Starch, WS (A – C), Rice Starch, RS, (D – F) and Corn Starch, CS (G – I) granules. A, D, G) 3D stacks; B – I) Cross-sections. Scalebar: 20 µm.

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