**Innovative strategies to modulate Delivery and Food Structuring abilities of Starch-based Ingredients**

Reindorf Boateng ([rboateng@unite.it](mailto:rboateng@unite.it))

Dept. Food Science and Technology, University of Teramo, Via R. Balzarini 1,64100, Italy

Tutor: Prof. Paola Pittia. Co-tutor: Dott. Marco Faieta

This PhD research project aims at applying an un-conventional physical technology, i.e. ball milling for the development of new starch ingredients with modified molecular properties and technological functionalities and their applications for food structuring and delivery systems. Different ball-milling process variables (rotation rate, time) will be tested on starches of different botanical origin (corn, potato, tapioca) and the corresponding chemical, physical, microstructural, and technological properties will be evaluated. Physically modified starches will be, then, used to design and develop delivery systems (e.g., emulsions, microencapsulates) and/or structures (cryogels) with new functionalities for innovative food systems applications.

**Strategie innovative per modulare le capacità di consegna e di strutturazione degli alimenti degli ingredienti a base di amido**

Questo progetto di ricerca di dottorato mira all’applicazione di una tecnologia fisica non convenzionale, ovvero la macinazione a sfere per lo sviluppo di nuovi ingredienti base amido con proprietà molecolari e funzionalità tecnologiche modificate e la loro applicazione come agenti strutturanti o in sistemi di rilascio. Verranno testate diverse variabili di processo della macinazione a sfere (velocità di rotazione, tempo) su amidi di diversa origine botanica (mais, patate, tapioca) e verranno valutate le corrispondenti proprietà chimiche, fisiche, microstrutturali e tecnologiche. Gli amidi modificati fisicamente saranno, quindi, utilizzati per progettare e sviluppare sistemi di stabilizzazione e rilascio (ad esempio emulsioni, microincapsulati) e/o strutture (criogel) con nuove funzionalità per applicazioni innovative in sistemi alimentari.

# **1. State-of-the-Art**

Starch is a natural biopolymer found in cereals and many plants-based products. It is made of glucose units organised in a complex multi-scale structure resulting from the arrangement of amylose and amylopectin. There is an increasing demand and importance of starch in food applications due to its interesting properties that contribute to the appearance, structure, and quality of the products. However, in its native state, starch has certain limitations that restrict its use. These limitations include poor solubility in cold water and its inability to withstand harsh processing conditions (e.g. high temperature) long hydration and swelling time, and tendency towards retrogradation. To overcome these issues, technologies to modify it have been developed by using physical, chemical, enzymatic methods, or combinations thereof (Baranowska and Kowalczewski, 2022) that result in improved technological properties (e.g., solubility, water, and oil binding capacity).

Physical technologies such as high pressure (HPP & HPH), cold plasma, pulsed electric field, and ball milling are being increasingly utilized for starch modification. These environmentally friendly techniques with wider consumer acceptance show great potential for producing ingredients with enhanced functionality in foods and allow manufacturer to avoid the “modified starch label designation”. Ball milling as an emerging and “green” technology is used as a physical processing method to modify starch. Recent studies demonstrated for its ability to enhance the properties and functionalities of the processed materials (Bangar *et al.*, 2023). Some authors (Huang *et al.*, 2008; Juarez-Arellano *et al.*, 2021) have reported on the use of ball milling for starch modification and their studies revealed improved amylose content, greater cold-water solubility, and lower temperature of gelatinisation.

In food industry various are the applications of starch, as both native or modified and among others, the ones growing interest relate to encapsulation and the development of gel-like structures. For instance, this biopolymer can form V-type inclusion complexes with tiny hydrophobic molecules (e.g., lipophilic vitamins, flavours, phenolics) within the inner helical cavity of amylose (Zhang *et al.*, 2023, Zhou and Kong, 2023). The growing use of "gel" structures in the food sector is driven by their advantages in terms of cost, availability, and digestibility. In fact, after gelatinisation and cooling, starch can reform an ordered structure (retrogradation) leading to the formation of three-dimensional network (hydrogel) with interesting properties and applications. Starch-based aerogels and cryogels, highly porous matrices obtained via starch dissolution and drying by supercritical CO2 or freeze-drying respectively, are increasingly used for both food and non-food delivery purposes (Cuo *et al*., 2021, Zou & Budtova, 2021). Eventually, starch granules represent a natural nontoxic emulsifier for particle-stabilised emulsified systems (Pickering emulsions), characterised by excellent long-term stability against coalescence.

In the field of starch-based materials, despite data available in the literature, a significant research gap still exists on the development of starch-based structures, in particular the more innovative ones (gels), and the technological functionality of ball-milled starch, as well as their application for encapsulation of lipophilic and hydrophilic compounds by conventional and/or innovative (i.e. co-milling) purposes, along with their potential ability for stabilizing Pickering emulsions.

# **2. PhD Thesis Objectives and Milestones**

Within the overall objective mentioned above this PhD thesis project can be subdivided into the following activities according to the Gantt diagram given in Table 2:

A1) **State-of-the art** **and methods of optimisation**. Literature review on starch, modifications by physical processes and technological functionality. Optimisation of methods for the evaluation of physical, microstructural properties and technological functionality (A1.1) (e.g., water solubility and swelling power, water and oil absorption test, microstructure, rheological and thermal behaviour).

A2) **Ball-milling (BM) starch modification:** Different process conditions on starch of different origin (corn, potato, and tapioca) will be applied: (time, rotation rate); processed BM starches will be characterised for morphological, physical (A2.1), technological functionality and stability (A2.2)

A3) **Design and development of BM-starch structures:** In this task, hydrogel and cryogel structures will be prepared and characterised. Hydrogels will be prepared by using selected BM-modified starch at different process time (5,15,30 min) and heated at 90 ºC. Their corresponding physical and functional characteristics will be determined (textural, thermal, crystallinity, granular morphology, retrogradation). Cryogels will be obtained by freeze-drying and characterized for density, porosity, moisture sorption isotherm, thermal properties, granular morphology, textural analysis, absorption capacity, crystallinity, mechanical properties.

A4) **Design and development of BM-based microencapsulates and structures as delivery systems**: Microencapsulated powders will be obtained by co-milling of mix of starch and lipophilic compounds and by Pickering emulsions and spray-drying. Complex gel structures (hydrogels, cryogels) will be developed by using BM-starches in presence of **other co-solutes and bio-actives of interest (e.g., oleuropeins, β-carotene)** Physical and microstructural properties along with digestibility and in-vitro bioavailability, release rate of the encapsulated selected compounds will be studied.

A5) **Writing and Editing** of the PhD thesis, scientific papers and oral and/or poster communications.

***Table 2***Gantt diagram for this PhD thesis project.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Activity Months | | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** | **13** | **14** | **15** | **16** | **17** | **18** | **19** | **20** | **21** | **22** | **23** | **24** |
| A1) | ***State-of the art and methods of optimisation*** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 1) Physical and microstructural properties |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 2) Technological functionality |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| A2) | ***Ball-milling starch modification*** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | 1) Technological functionality |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| A3) | ***Design and development of BM-starch structures*** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| A4) | ***Design and development of BM-based microencapsulates and structures as delivery systems*** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| A5) | ***Thesis and Paper Preparation*** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

# **3. Selected References**

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