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## Future-proofing dietary pea starch

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14	The demand for protein concentrates/isolates from field peas (Pisum sativum L.) has steadily increased
15	along with the market of plant-based meat alternatives and the increased awareness of the poor
16	environmental footprint and perception of soy beans. Although pea protein-based structures are softer
17	that those from soy, appealing factors such as price, sustainability, availability and easy incorporation
18	into plant-based food recipes, make field pea a leading crop for plant-based food applications. For all
19	the above, pea starch, accounting for about 50 % of the dry seed mass, is considered more than ever
20	before an abundant by-product from the fractionation of peas, and a relatively cheap starch in
21	comparison to wheat, corn, and potato starches, that should be taking central stage. Nevertheless, why
22	the demand for pea starch is unpaired with its abundance? Why is not pea starch as ubiquitous as its
23	protein counterpart in plant-based foods and/or starchy foods? Amylose leads the answer.
24	Inclination towards clean label, healthy-eating, sustainability and convenience can fuel the growth of
25	the global pea starch market. However, future-proofing pea starch composition, structure and
26	functionality will be paramount for a long-term business growth. Both of the most common dietary
27	phenotypes of P. sativum L., smooth and wrinkled pea, yield starch with relatively low contents of
28	endogenous lipids and, most importantly, a distinctively high amylose to amylopectin ratio (30-50 and
29	60-80% for smooth and wrinkled pea, respectively). Moreover, pea starch amylose seems to exhibit a

higher relative amount of a population of short amylose chains of approximately 250 glucose units than that from cereal and tuber starches (Fig. 1)<sup>1</sup>. As a consequence of some (or all) of these features, the amylose-driven strong gelling capacity makes pea starch ideal for edible coatings in deep-fried or microwaved foods <sup>2</sup>, and for any other applications where chewiness and cohesiveness are desired (e.g., meat products and glass noodles). However, pea starch is not suitable as thickening agent for the vast majority of food products due to its low (pasting curve without visible peak viscosity) and slow (increasing viscosity during the holding period) granular swelling<sup>2</sup>. Pea starch is neither suitable for applications where excessive gel syneresis and stiffness must be avoided due to its extraordinary high tendency to form stiff gels upon gelatinization and retrogradation<sup>1,2</sup>. This situation becomes even more dramatic in the wrinkled pea phenotype, where starch granules have negligible swelling unless cooked under pressure, similarly to high amylose maize starch, and results in very stiff gels upon retrogradation<sup>2</sup>. All in all, an improved demand for pea starch as food ingredient will have to arise from or grafted attributes that complement its price, abundance and hypoallergenicity.

## STANDARIZATION OR DIFFERENCIATION?

The removal of the amylose-driven shortcomings could standardize the swelling and retrogradation behavior of pea starch to that of other starches<sup>2</sup>. Nevertheless, its amylose-rich composition can become a double-edged sword in the search for novel human and environmental health solutions. Firstly, high amylose wrinkled pea phenotypes have been shown to provide further advantages of pea starch in a view to closing the fiber gap<sup>3</sup>. Different from smooth pea and similar to high amylose starches, granular wrinkled pea starch possesses a B-type crystalline pattern, typically categorized as Resistant Starch (RS) which is, in turn, retained during thermal events such as baking. Even if fully gelatinized, wrinkled pea starch is susceptible to form complexes with free lipids or form double-helical structures through amylose retrogradation, both resistant to  $\alpha$ -amylase digestion, becoming also a promising fiber-rich ingredient in extruded ready-to-eat cereals, snacks, or foods that need to be further re-heated. Moreover, amylose-driven RS can be easily quantified using standardized and harmonized *in vitro* digestion methods, including the official methods already implemented for the measurement of the contents of dietary fiber and RS<sup>4</sup>. Therefore, wrinkled pea starch has the additional advantage of being accounted for by food labels, which could provide opportunities for prospective health claims on RS. Secondly,

field pea starch has a remarkable and unexploited potential to become a source of spherical and tight sub-micron size particles (nanoblockets) resulting from the presence of alternating amorphous and nanocrystalline domains and an amylose-rich granular composition. Regardless of the /isolation synthesis pathway of starch nanoparticles (e.g. anti-solvent precipitation), amylose, with much smaller molecular weight than amylopectin, tends to form smaller and tighter nanoparticles, with greater shear tolerance, thermal stability and ability to form inter-particulate networks (of greater viscosity) than amylopectin does<sup>5</sup>. Field pea starch nanoparticles could become excellent plant-based regulators of the mechanical strength and barrier properties of food and/or polymeric systems (e.g. food gels, bio-based packaging), carriers of nutrients (e.g. food metabolites, drugs), and octenyl succinic anhydride (OSA)-free starch-based stabilizers of food colloidal systems (e.g. Pickering stabilizers with enhanced surface hydrophobicity and small size for fine food emulsions).

## **FUTURE OUTLOOK**

Whether pea producers should aim for the removal of amylose-driven shortcomings (standardization to commonly used starches) or further exploitation of its "amylotype" similarities (differentiation) will depend on the targeted use. Looking ahead, one may assume that the exploitation of field pea starch and the journey to explore new markets for the pea starch co-product will remain an important area of research. From a fundamental research perspective, understanding the generation of homozygous null genotypes for the development of high amylose pea starches will remain one of the most appealing topics. In this regard, prospective breeding strategies to modify starch biosynthesis will have to be framed within the context of making more protein-packed peas, responding to the looming question of how to feed our growing population. With or without modified starch biosynthesis, green chemistry and processing approaches to manipulate the particle size, wettability, aggregation and surface chemistry that result in the ultimate pea starch-based colloid/biomaterial, will spearhead the efforts in the upcoming years. The crossover between the genetic nature of protein concentration and amylose ratio, as well as fine modification technologies, could result in an outstanding source of building blocks of function from this cool-season crop that can tolerate low temperatures and high latitudes for germination and growth.

## **COMPETING INTERESTS**

- 86 The authors declare no competing interests.
- 87 FIGURE CAPTIONS
- 88 Figure 1. Size exclusion chromatograms of debranched starch samples from common sources. The
- small size population of pea amylose branches is tinted in light yellow. Based on data by Martinez, et
- 90 al.<sup>1</sup>.
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