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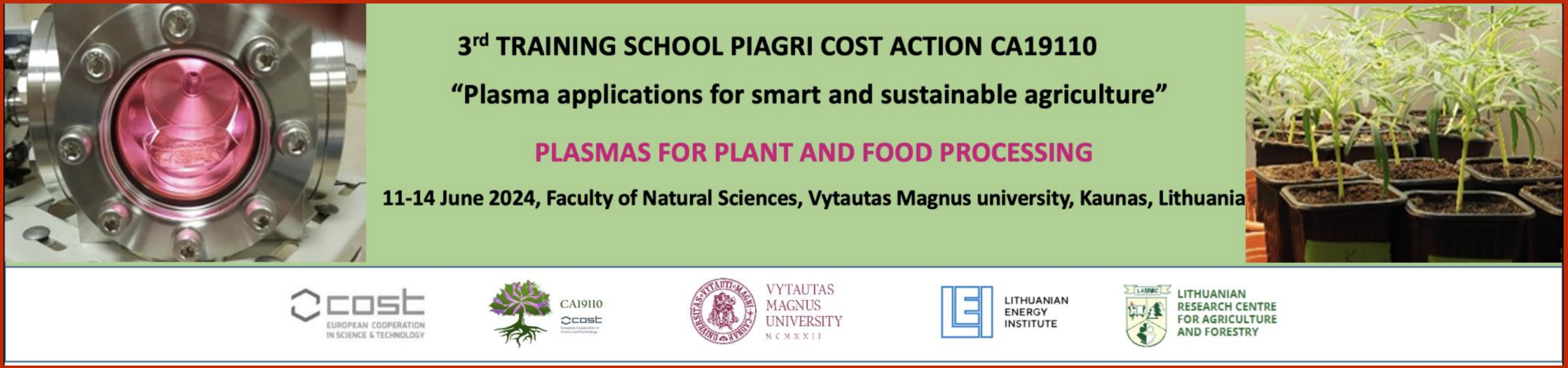

'Application of cold plasma for the functionalization of food ingredients'

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Technological functionality: what do we intend?

Physical and chemical properties which affect the behavior of components in food systems during processing, storage, preparation, and consumption

Fundamental in Food Formulation and innovation

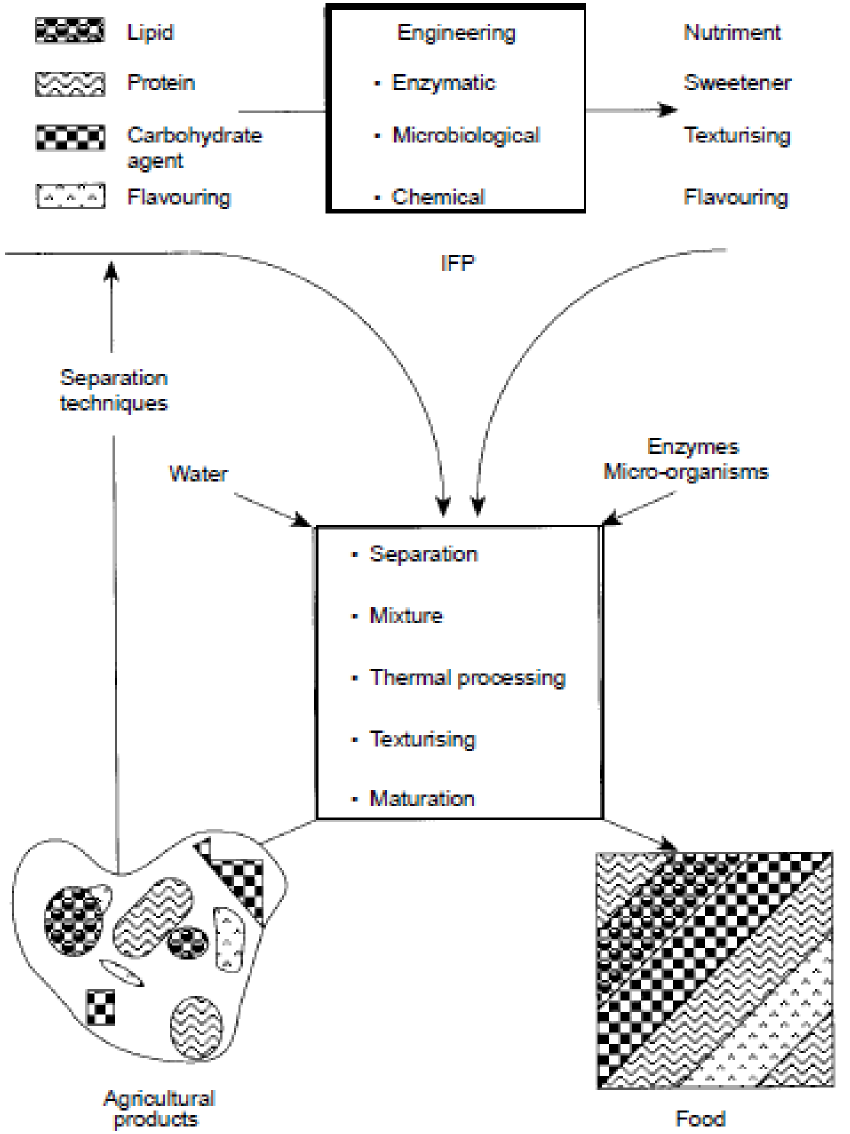
Intermediate Food Product (IFP) concept

types of processed materials with distinct characteristics, used with increasing flexibility and with increasing refined functional properties

Challenge for the industry:

achieve improvements to agricultural commodity constituents that vary over time and are often difficult to store.

Eg: waste products from the food industry can become bases for new ingredients, whose constituents (e.g. casein and whey, blood, etc.) need to be refined for further uses



Functionalities of food ingredients

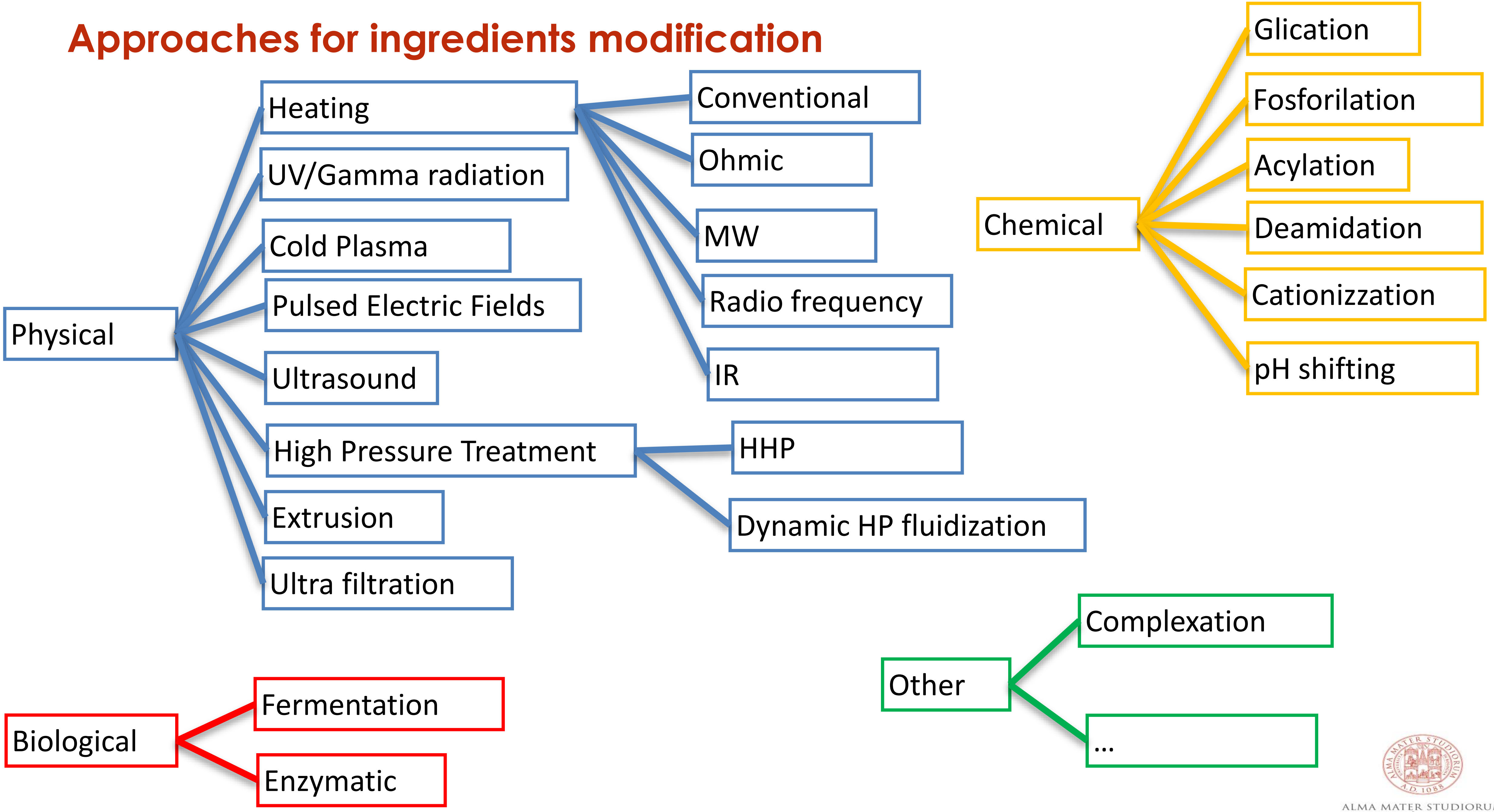
- ability to bind and adsorb water,
- emulsifying capacity,
- thickening capacity,
- adhesive capacity,
- dispersive capacity,
- solubilizing capacity,
- gelling capacity,
- foaming capacity,
- ability to bind aromas
- ability to release aromas,
- sweetening capacity,
- acidifying capacity,
- flavoring capacity,
- ability to lower water activity,
- ability to raise the glass transition temperature
- antioxidant property
- antimicrobial properties

Why modifying ingredients?

Challenges of native ingredients →

Poor solubility
High variability and low standardization
Sensibility to environmental stress conditions
Poor techno-functional properties
Undesirable flavours
digestibility

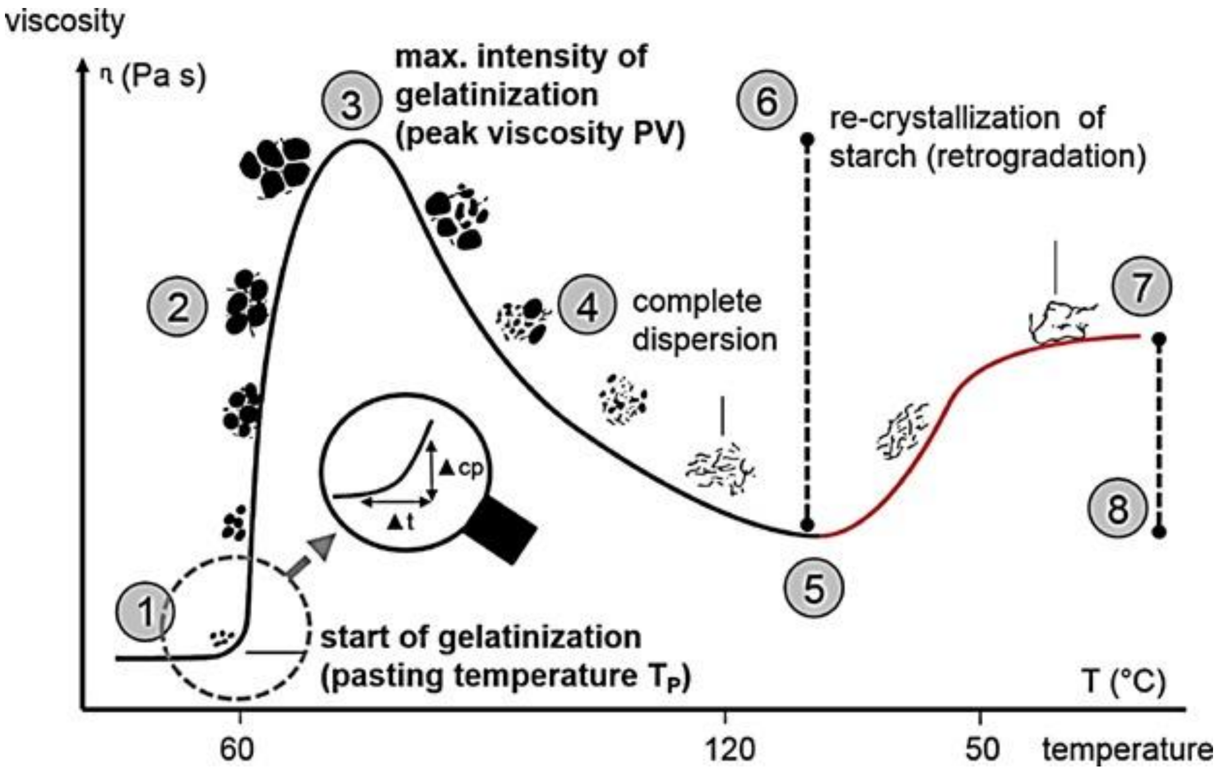
Approaches for ingredients modification



Starches used as ingredients

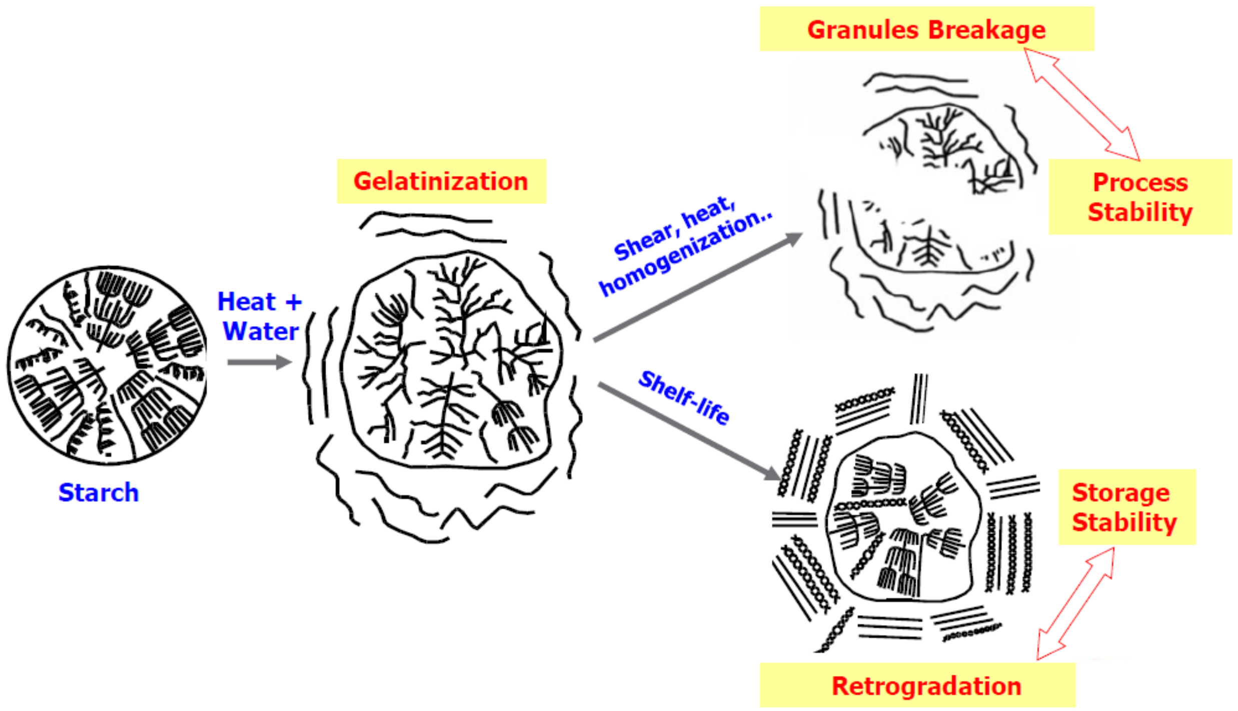
Functionalities of starches:

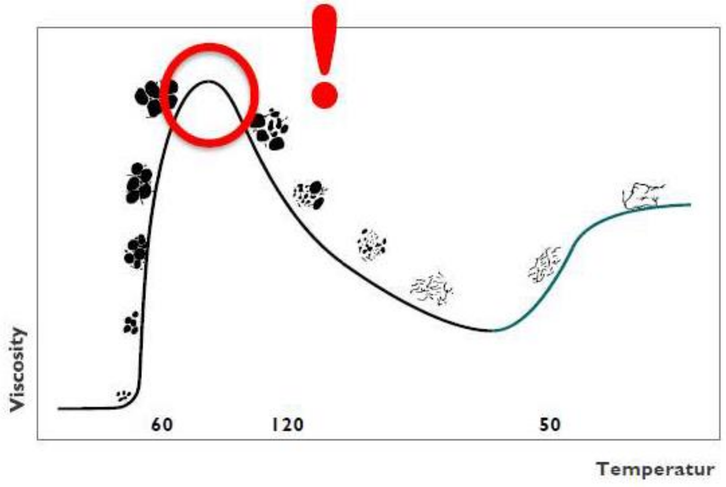
Thickeners, add moisture, elasticity and texture to bakery products, binding abilities, coating, development of crust in baked goods, ...



Starch gelatinization and retrogradation
in relation to viscosity

Native starches and their limitations





- Narrow peak viscosity range
- Little process tolerance
- Undesirabel texture
- Poor qulity of final products
- Short shelf-life stability

1. Process Resistance (starch granules damage)

- Heat Treatments (pasteurization, retorting, pasteurization after cooking and cooling…)
- Shear (cutters, colloid mill, homogenizers….)
- Acidic pH

2. Shelf-life Resistance (retrogradation/syneresis)

- Retrogradation, Syneresis, Texture changes during shelf-life
- Freeze/Thaw resistance

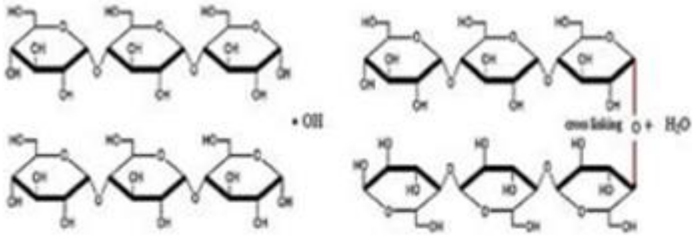
Examples of modification of starches by Cold Plasma

Starch	Plasma parameters	Starch parameter	Results
Potato, corn, wheat, rice	Ethylene gas, 65 kV	Reducing sugars	Increased
Rice	Air, 40 & 60 W	Starch hydrolysis	Decreased
Potato, corn, wheat, rice	Air , 1–2 kV	Water content	Decreased
Tapioca	Argon gas, 50 W	Paste clarity	Increased
Potato, corn, wheat, rice	Oxygen gas, 65 kV	pH	Decreased
Potato	Nitrogen gas, 245 V	Retrogradation	Decreased
Rice	Air, 40 & 60 W	Swelling power	Increased
Potato, corn, wheat, rice	Air, 1–2 kV	Iodine complex	Decreased
Wheat	Oxygen gas, 800 V	Polarity	Decreased
Rice	Air, 40 & 60 W	Syneresis %	Increased

Cold Plasma: an Alternative Technology for the Starch Modification
(Thirumdas et al., 2017)

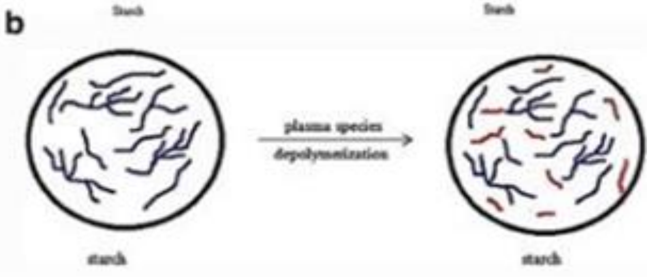
Corn starch treatment by super-arc plasma
20, 22, 24, 26, and 28 kV
1, 3, 5, 7, and 9 min
1, 2, 3, 4, and 5 g

Laricheh, R., Fazel, M., & Goli, M. (2022). **Corn starch structurally modified with atmospheric cold-plasma and its use in mayonnaise formulation.** *Journal of Food Measurement and Characterization*, 1-14.



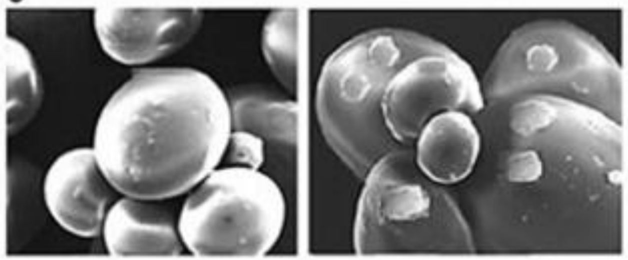
Cross-linking of starch branched chains

b



Depolymerization

c



Etching starch granules

Parameter	Type	Treated with cold plasma	Control
Water adsorption (%)	Starch	48.29 ± 4.25^{a}	27.93 ± 2.25^{b}
Oil absorption (%)		1.77 ± 0.19^{a}	1.29 ± 0.15^{b}
Solubility (%)		15.60 ± 0.76^{a}	7.94 ± 0.88^{b}
Stiffness (g)	Starch gel	189.47 ± 2.20^{a}	163.66 ± 1.15^{b}
Cohesiveness (–)		0.857 ± 0.02^{a}	0.869 ± 0.08^{a}
Elasticity (–)		0.922 ± 0.08^{b}	0.996 ± 0.05^{a}
Gumminess (g)		139.28 ± 2.34^{b}	142.28 ± 1.21^{a}
Resistance (g/sec)		110.05 ± 7.42^{b}	123.14 ± 8.45^{a}
Intrinsic viscosity (cp)		141.7 ± 3.20^{b}	185.16 ± 3.20^{a}

Case study: Application of PAW for the modification of starches

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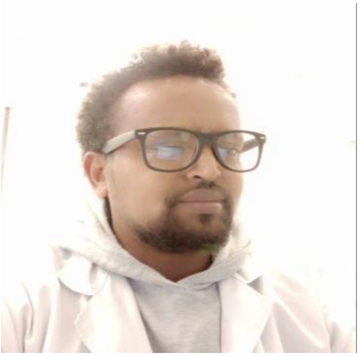
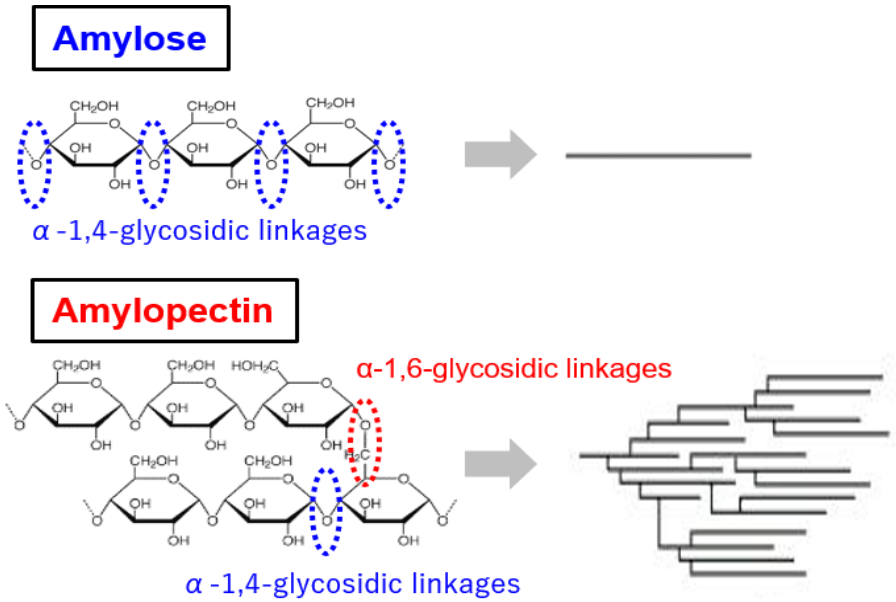


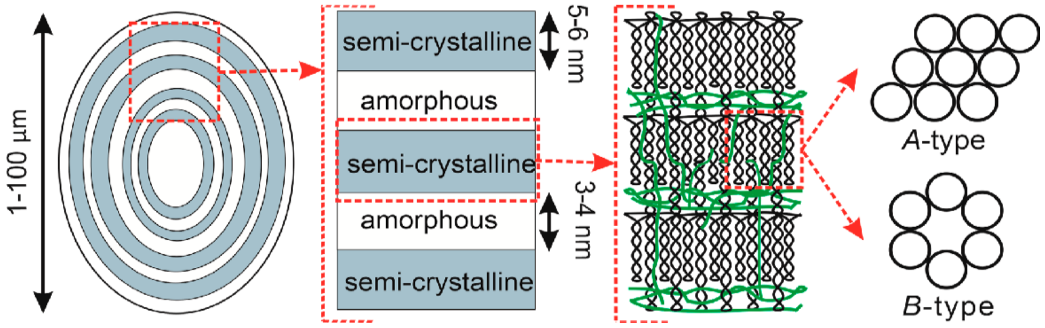
Specific Objectives

1. Effects of **Plasma Activated Water (PAW)** on Rheological, Thermal, Hydration and Pasting Properties of **Normal Maize, Waxy Maize and Potato starches**
2. Effects of Incubation Time of **Plasma Activated Water (PAW) Combined to Annealing** for the Modification of Functional Properties of Potato Starch
3. Plasma-Activated Water (PAW) and Annealing for the modification of potato starch: Effects on **Sorption Isotherms, Thermodynamic and Gelatinization Kinetics** of Potato Starch

Selection of starches



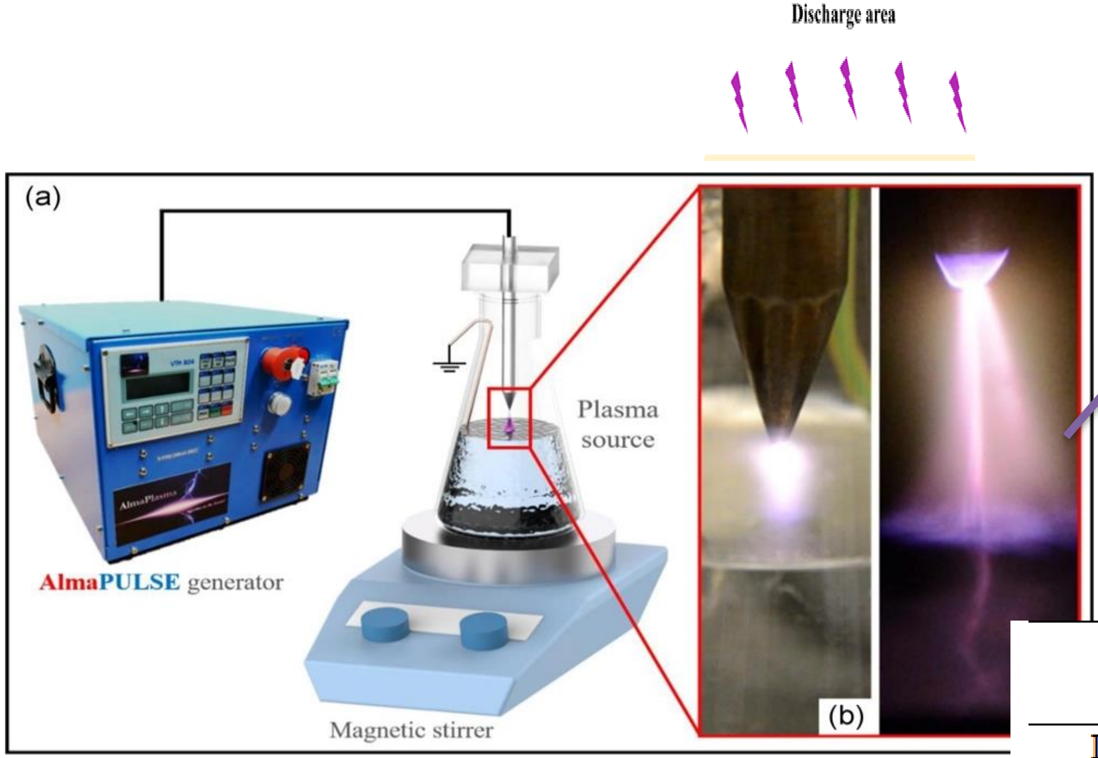
Type	Tuber **Potato** B type	Cereals **Normal Maize** A type	 **Waxy Maize** A type
Amylose (%)	20	25	<1
Amylopectin (%)	80	75	>99
Size (µm)	15-100	5-26	5-26
Shape	Oval, Spherical	Round, Polygonal	Round, Polygonal

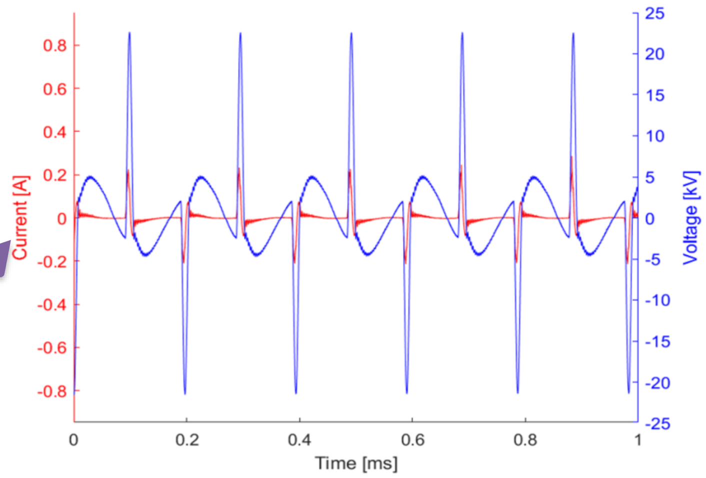


Specific objective 1

Generation of PAW

V =15kV
f = 5kHz
At= 60s
VDW= 500ml





Av. Discharge power: 167.12 ± 12.42 W

Sample	NO_2^- [mg/l]	H_2O_2 [mg/l]	pH
DW	0	0	6.12 ± 0.05
PAW	13.98 ± 3.47	1.18 ± 0.06	3.48 ± 0.08

Starches:
- Potato
- Normal Maize
- Waxy Maize

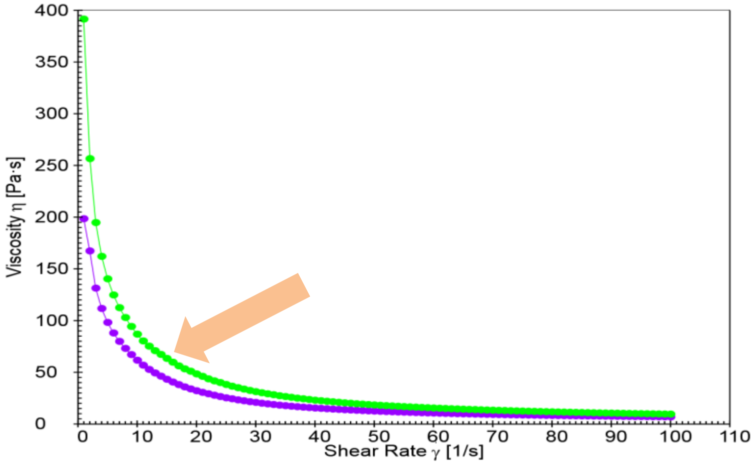
Mixture starch:water/PAW 1:2
Continuous mixing for 20 min
Drying in oven at 40°C

- Rheological behaviour
- Pasting Properties
- Hydration properties

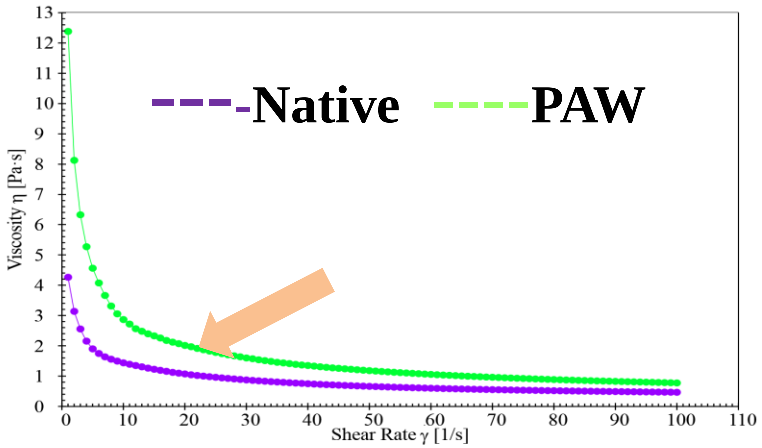
Rheological behaviour

steady shear behaviour

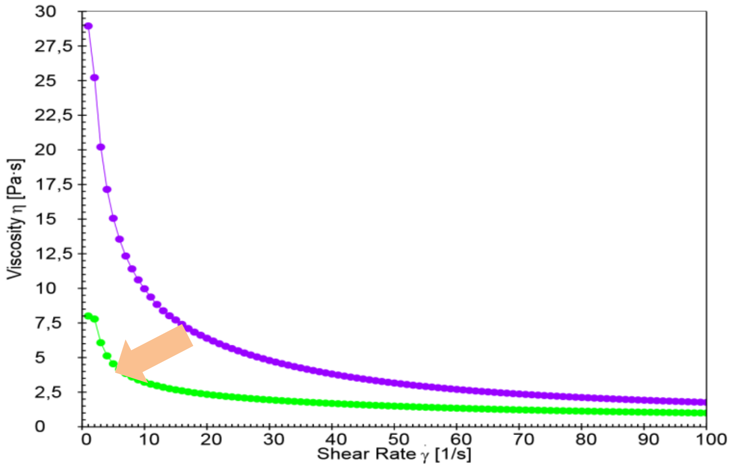
Potato



Normal Maize



Waxy Maize



Power law

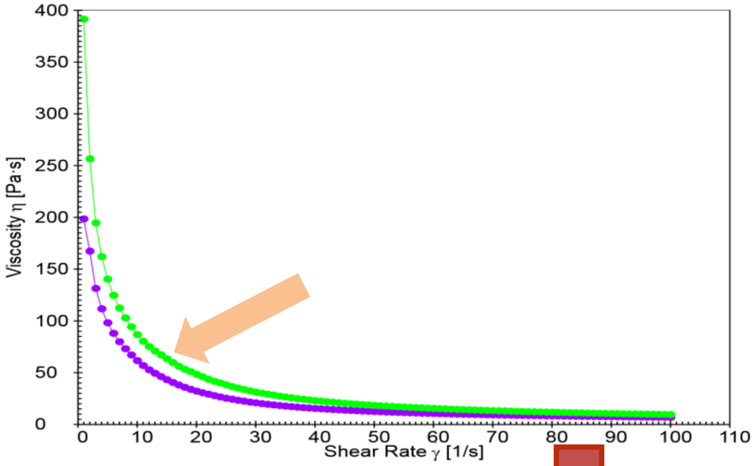
$$\tau = K\,\dot{\gamma}^{n}$$

Sample		K (Pa·s^n)	n	R^2
P	Native	47.91±0.12^b	0.50±0.03^a	0.99
	PAW	88.74±1.14^a	0.44±0.02^b	0.99
NM	Native	11.7±0.64^b	0.46±0.01^a	0.99
	PAW	58.56±2.42^a	0.24±0.01^b	0.95
WM	Native	6.85±0.59^a	0.38±0.01	0.99
	PAW	4.63±0.18^b	0.39±0.01	0.99

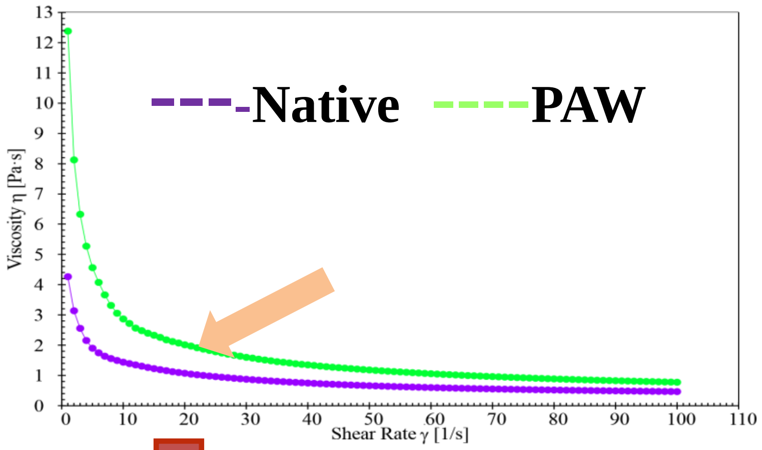
Rheological behaviour

steady shear behaviour

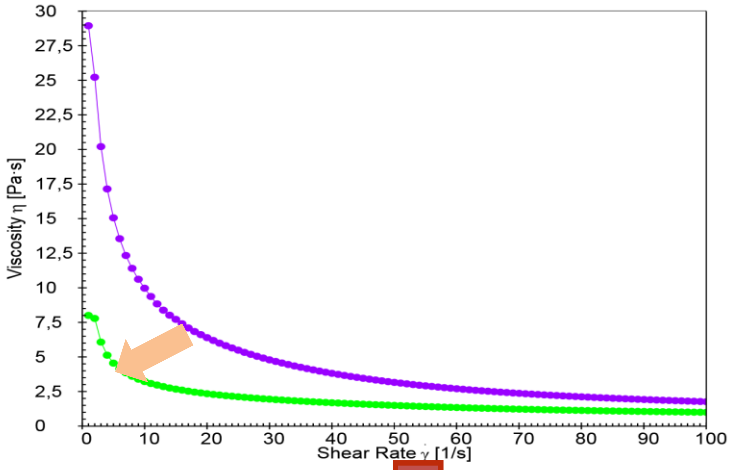
Potato



Normal Maize



Waxy Maize



- INCREASED CONSISTENCY COEFFICIENT
- HIGHER G' AND G''

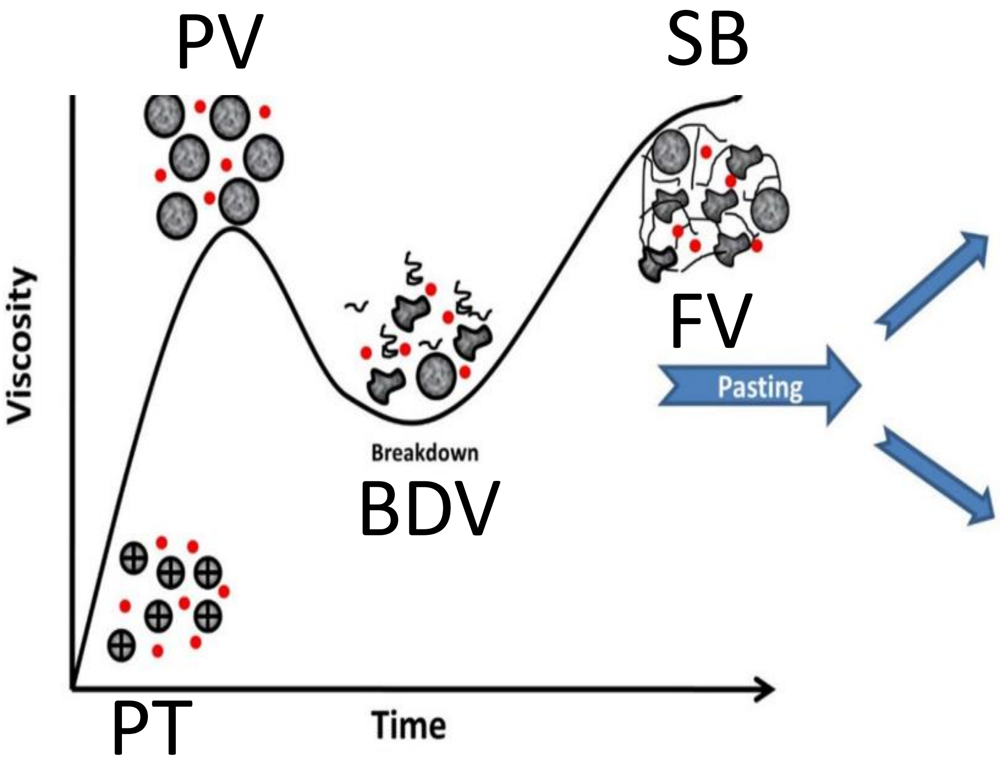
Hypothesis:
reduction of hydroxyl of groups in the starch structure due to the reactive species in PAW, such as O3, an entanglement of the starch structure which improved the ability of starch to combine with water

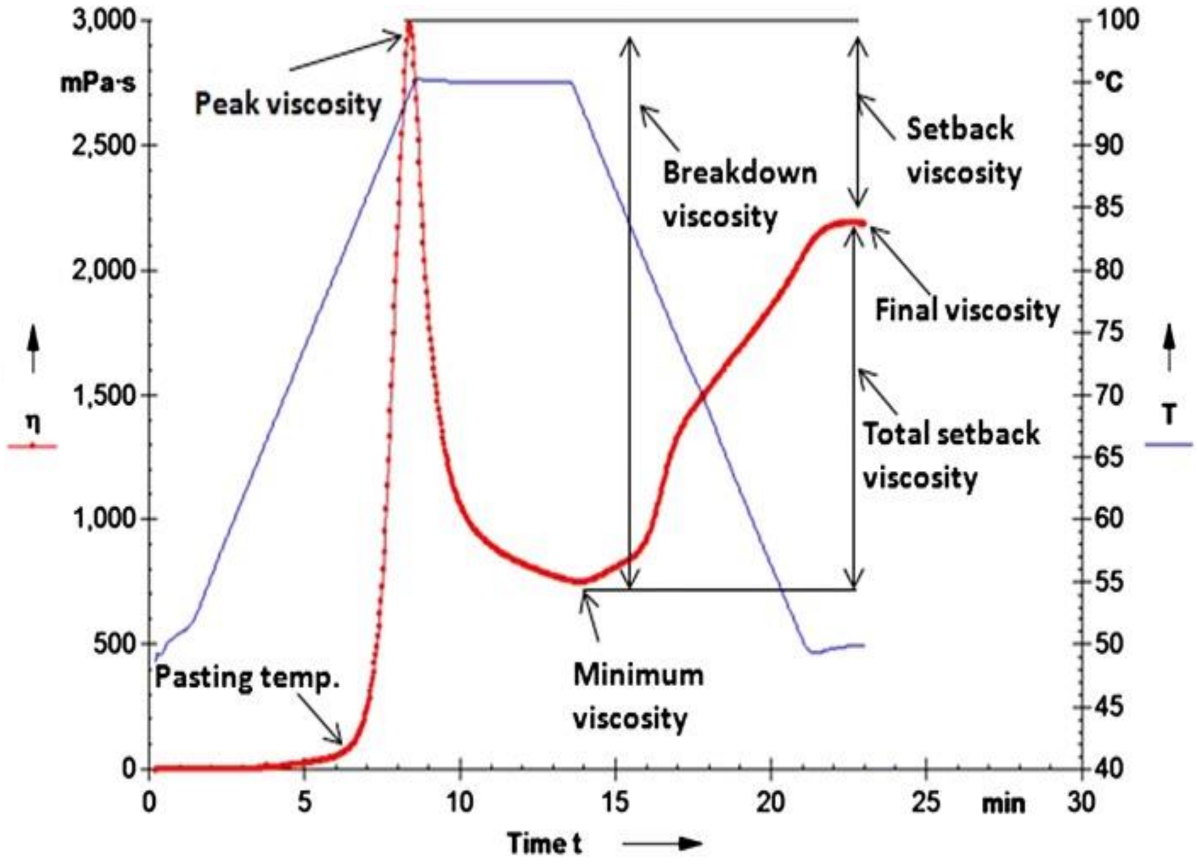
- DECREASED CONSISTENCY COEFFICIENT
- LOWER G' AND G''

Hypothesis:
dissociation (rupture of glycosidic bonds) of double helices of amylopectin and reduced granule crystallinity
depolymerization effect

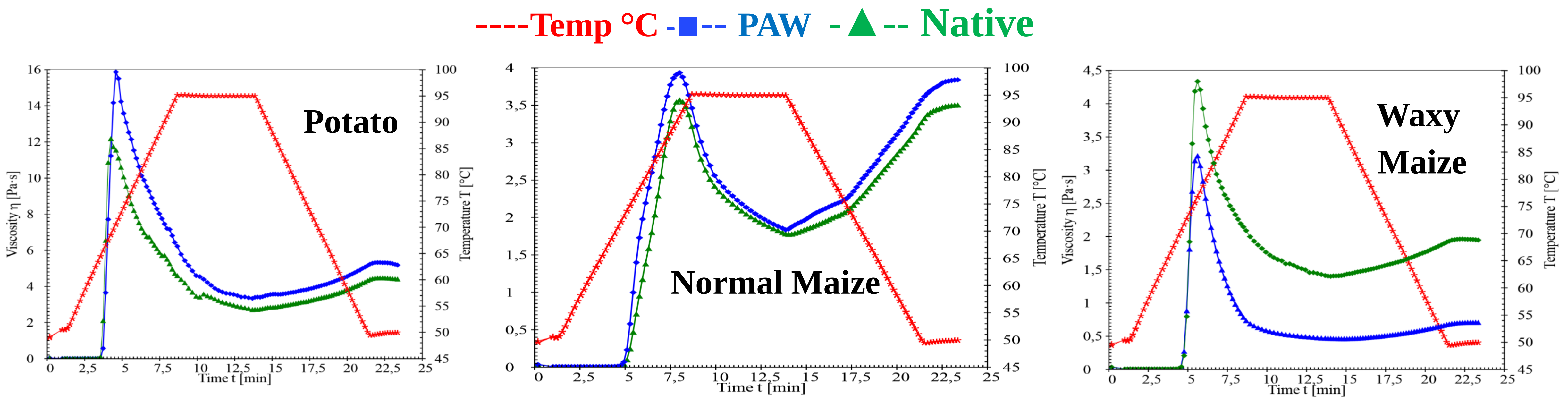
Main difference between WM and other starches: content of amylose (almost absent in WM)

Pasting properties





Pasting proerties



Sample		PT (°C)	PV (Pa.s)	HSV (Pa.s)	BV (Pa.s)	SBV (Pa.s)	FV (Pa.s)
P	**Native**	64.19±0.68[b]	12.34±0.19[b]	2.73±0.01[b]	9.61±0.20[a]	1.73±0.14	4.46±0.14[b]
	PAW	65.05±0.60[a]	15.78±0.9[a]	3.26±0.10[a]	12.52±0.03[b]	1.9±0.07	5.16±0.03[a]
NM	**Native**	75.54±0.95[a]	3.67±0.19	1.78±0.04	1.88±0.15[b]	1.78±0.13	3.57±0.17
	PAW	71.72±0.22[b]	3.85±0.17	1.83±0.02	2.02±0.15[a]	1.92±0.14	3.75±0.16
WM	Native	70.72±0.20	4.25±0.12[a]	1.37±0.03[a]	2.87±0.10	0.55±0.02[a]	1.93±0.04[a]
	PAW	70.63±0.25	3.22±0.18[b]	0.46±0.07[b]	2.75±0.13	0.24±0.03[b]	0.71±0.10[b]

Conclusions – 1

Observed modifications: attributed to the synergistic effect of NO_3, NO_2, O_3, acidic environment, and other reactive species of PAW

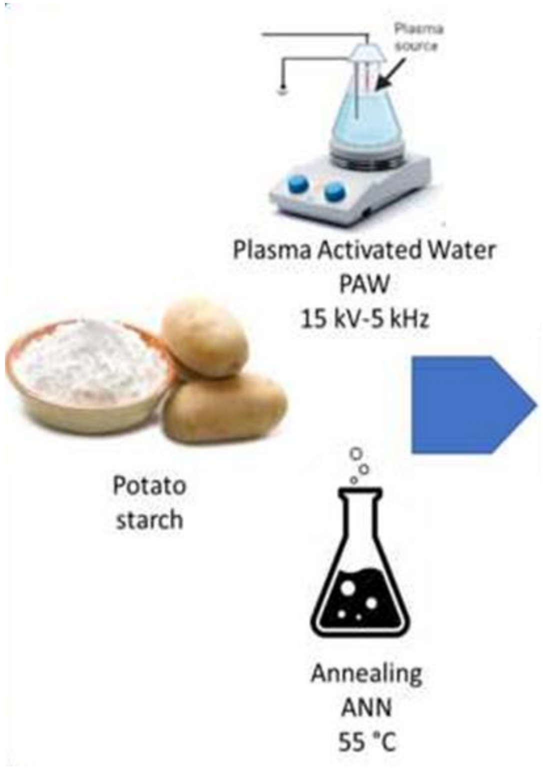
Cereal and tuber/roots starches can be successfully modified by PAW ➔ promising strategy for starch modification as “green” alternative for existing methods in the food industry

Degree of modification: strongly dependent on the starch type (botanical, amylose, and amylopectin content) ➔ process optimization based on the specific substrate appears necessary for obtaining tailored functionality

Combination of PAW with annealing

What is annealing?

physical reorganisation of starch granules (or appropriate polysaccharide matrices like amylose–lipid complexes) when heated in excess of water (or appropriate plasticiser) at a temperature between T_g and the onset of gelatinisation (T_o) of the native starch (or polymeric system)

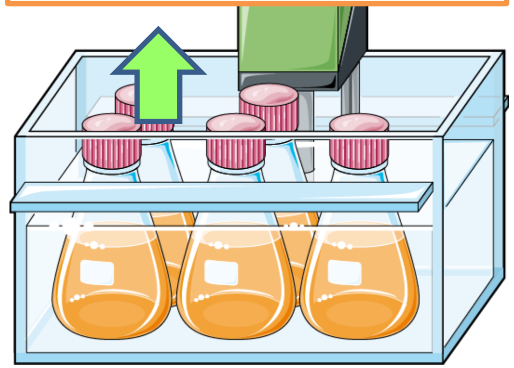


Requires long time ➔ combination with PAW?

PAW
ANN
PAW +ANN

Ratio Starch/PAW: 1/2

1, 4, 8 and 12 hours

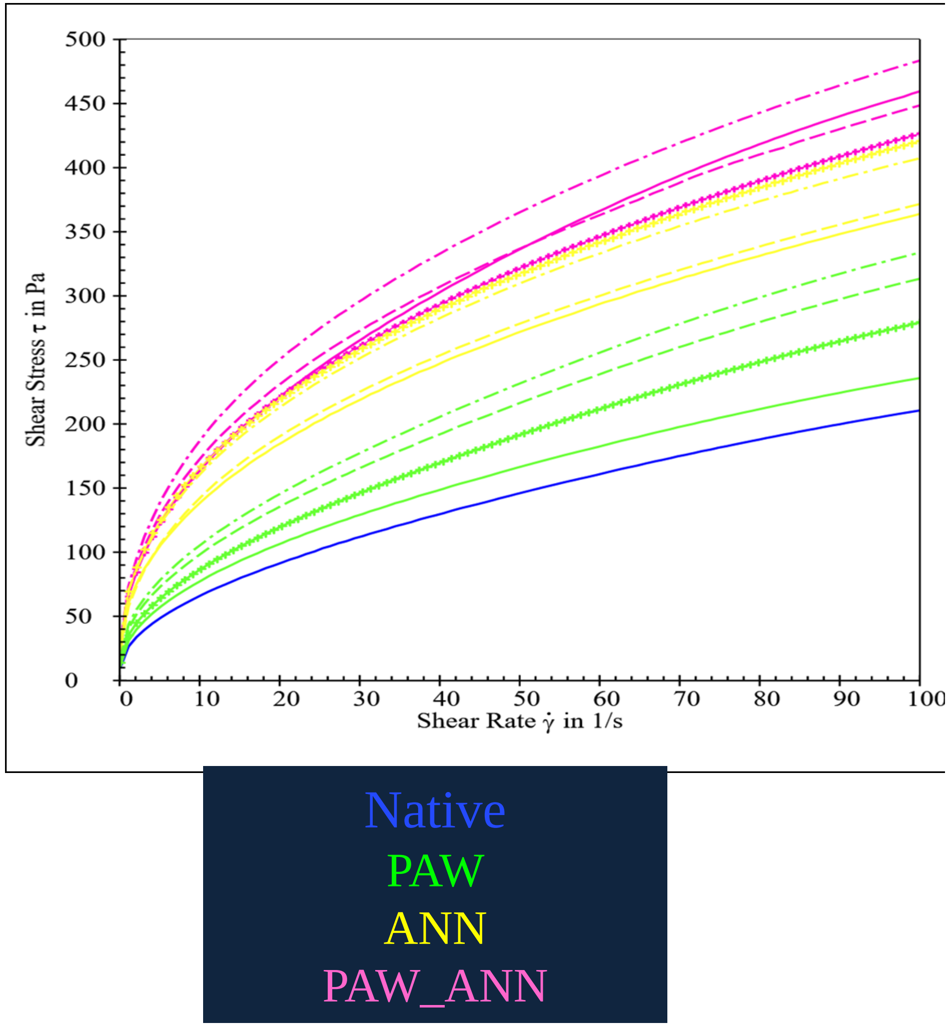


Effect on:

- Rheological
- Thermal
- Pasting
- Hydration

Properties

Rheological behaviour



$$\tau = K\,\dot{\gamma}^{n}$$

Sample	Incubation time (h)	K	n	R^2
Native	-	23.25±0.31[j]	0.47±0.007[a]	0.991
PAW	1	30.64±0.22[g]	0.47±0.005[ab]	0.989
	4	37.95±0.26[i]	0.47±0.003[a]	0.991
	8	35.25±0.29[h]	0.47±0.005[ab]	0.990
	12	34.83±0.26[h]	0.47±0.004[ab]	0.999
ANN	1	46.28±0.39[c]	0.45±0.001[abc]	0.999
	4	50.74±0.60[e]	0.43±0.01[bcd]	0.999
	8	55.05±1.32[e]	0.44±0.001[abcd]	0.999
	12	55.25±0.60[e]	0.41±0.003[d]	0.999
PAW-ANN	1	60.88±0.75[c]	0.44±0.004[bcd]	0.990
	4	66.07±0.53[b]	0.42±0.003[d]	1.000
	8	70.96±0.54[a]	0.42±0.003[cd]	0.990
	12	63.85±0.01[b]	0.41±0.001[d]	0.999

Specific objective 2

Rheological behaviour

$$\tau = K\,\dot{\gamma}^n$$

INCREASED CONSISTENCY COEFFICIENT

PAW ➔ reassociation of starch chains, following reduction of hydroxyl groups in the starch structure due to PAW reactive species, that enhanced the starch interaction

ANN ➔ more complete rearrangement of potato starch molecules, ➔ tighter and more organized molecular structures with more rigid and cohesive starch that is resistant to flow.

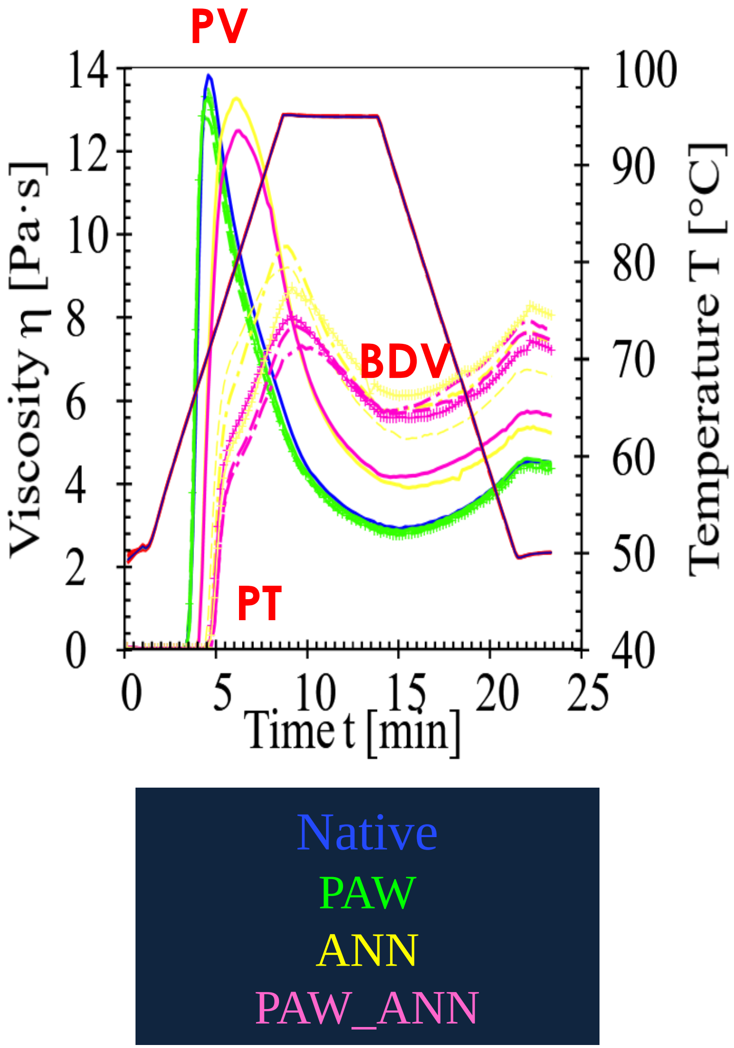
PAW-ANN ➔ synergistic effect

After only 1 h of PAW-ANN k values higher compared to the maximum value reached for the longest ANN treatment (12 h)

Sample	Incubation time (h)	K	n	R^2
Native	-	23.25 ± 0.31^{j}	0.47 ± 0.007^{a}	0.991
PAW	1	30.64 ± 0.22^{g}	0.47 ± 0.005^{ab}	0.989
	4	37.95 ± 0.26^{i}	0.47 ± 0.003^{a}	0.991
	8	35.25 ± 0.29^{h}	0.47 ± 0.005^{ab}	0.990
	12	34.83 ± 0.26^{h}	0.47 ± 0.004^{ab}	0.999
ANN	1	46.28 ± 0.39^{c}	0.45 ± 0.001^{abc}	0.999
	4	50.74 ± 0.60^{e}	0.43 ± 0.01^{bcd}	0.999
	8	55.05 ± 1.32^{e}	0.44 ± 0.001^{abcd}	0.999
	12	55.25 ± 0.60^{e}	0.41 ± 0.003^{d}	0.999
PAW-ANN	1	60.88 ± 0.75^{c}	0.44 ± 0.004^{bcd}	0.990
	4	66.07 ± 0.53^{b}	0.42 ± 0.003^{d}	1.000
	8	70.96 ± 0.54^{a}	0.42 ± 0.003^{cd}	0.990
	12	63.85 ± 0.01^{b}	0.41 ± 0.001^{d}	0.999

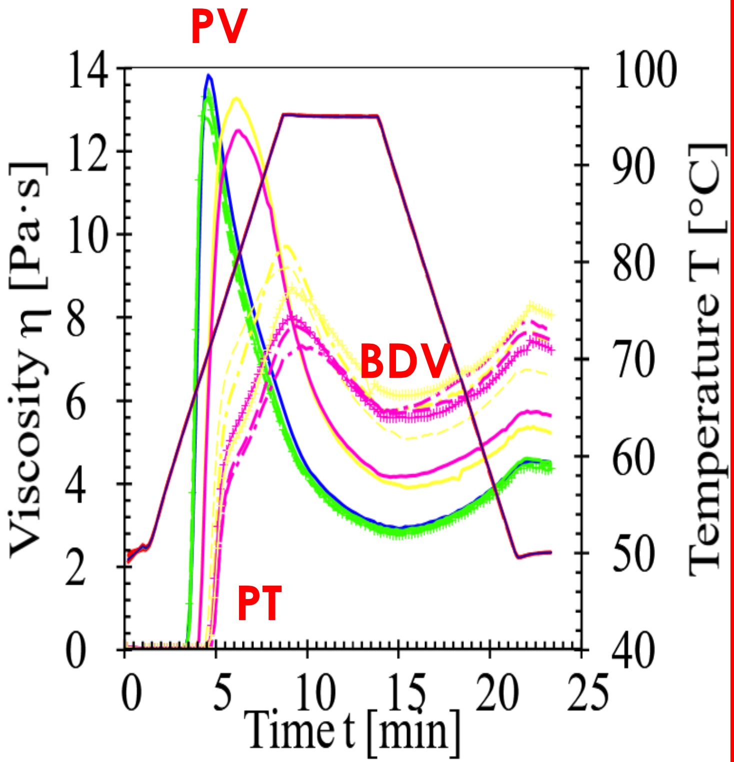
Specific objective 2

Pasting properties



Sample	PT(°C)	PV(Pa.s)	BDV(Pa.s)	HSV(Pa.s)	SBV(Pa.s)	FV(Pa.s)
Native	64.50±0.03^{e}	13.75±0.13^{a}	10.89±0.07^{a}	2.85±0.06^{d}	1.63±0.07^{ab}	4.49±0.01^{e}
PAW 1h	64.49±0.01^{e}	13.15±0.17^{ab}	10.33±0.17^{a}	2.82±0.03d	1.56±0.17^{bc}	4.38±0.14^{e}
PAW 4h	64.63±0.75^{e}	13.57±0.11^{ab}	10.75±0.13^{a}	2.82±0.01^{d}	1.61±0.05^{ab}	4.43±0.04^{e}
PAW 8h	64.99±0.69^{e}	12.83±0.07^{ab}	10.05±0.10^{a}	2.78±0.02^{d}	1.60±0.08^{abc}	4.38±0.06^{e}
PAW 12h	64.71±0.77^{e}	13.20±0.17^{ab}	10.45±0.16^{a}	2.75±0.02^{d}	1.58±0.01^{ac}	4.33±0.03^{e}
ANN 1h	68.05±0.74^{d}	12.56±1.00^{ab}	8.74±0.87^{b}	3.83±0.13^{c}	1.43±0.21^{c}	5.26±0.08^{d}
ANN 4h	70.11±0.76^{bcd}	9.16±0.09^{cd}	4.08±0.09^{c}	5.08±0.01^{a}	1.55±0.04^{bc}	6.63±0.05^{c}
ANN 8h	71.19±0.74^{abc}	9.77±0.07^{c}	4.14±0.11^{c}	5.64±0.03^{b}	1.59±0.29^{abc}	7.22±0.25^{b}
ANN 12h	72.21±0.72^{ab}	8.43±0.41^{de}	2.41±0.28^{d}	6.02±0.12^{a}	1.92±0.01^{a}	7.93±0.13^{a}
PAW_ANN 1h	68.78±0.3^{cd}	12.16±0.16^{b}	8.11±0.31^{d}	4.23±0.13^{d}	1.54±0.12^{c}	5.70±0.12^{d}
PAW_ANN 4h	72.30±0.42^{ab}	7.83±0.05^{e}	2.07±0.05^{d}	5.66±0.14^{a}	1.44±0.03^{bc}	7.21±0.03^{b}
PAW_ANN 8h	72.15±0.27^{a}	7.76±0.06^{e}	2.20±0.06^{d}	5.77±0.29^{a}	1.97±0.24^{abc}	7.75±0.05^{a}
PAW_ANN 12h	71.65±0.76^{ab}	7.89±0.30^{e}	2.31±0.28^{d}	5.57±0.02	1.62±0.17^{a}	7.57±0.18^{ab}

Pasting properties



Native
PAW
ANN
PAW_ANN

Peak Temperature (PT): resistance to swelling, agglomeration of starch granules, crystallinity index, level of cross-linking, and a reduction in the space between molecules

Increase ➔ rising in resistance to swelling, agglomeration of starch granules, increased crystallinity, development of intermolecular cross-links, reduction in the space between molecules which hinders the viscosity development during annealing.

Interaction between starch chains in the amorphous and crystalline regions ➔ starch more stable, needs a higher temperature for the rupture of the structure.

Peak viscosity (PV): measure of the fragility and the maximum degree of swelling of starch granules before disintegration when subjected to heating.

Decrease ➔ the binding forces within the granules were strengthened, limiting starch swelling and structural disintegration.

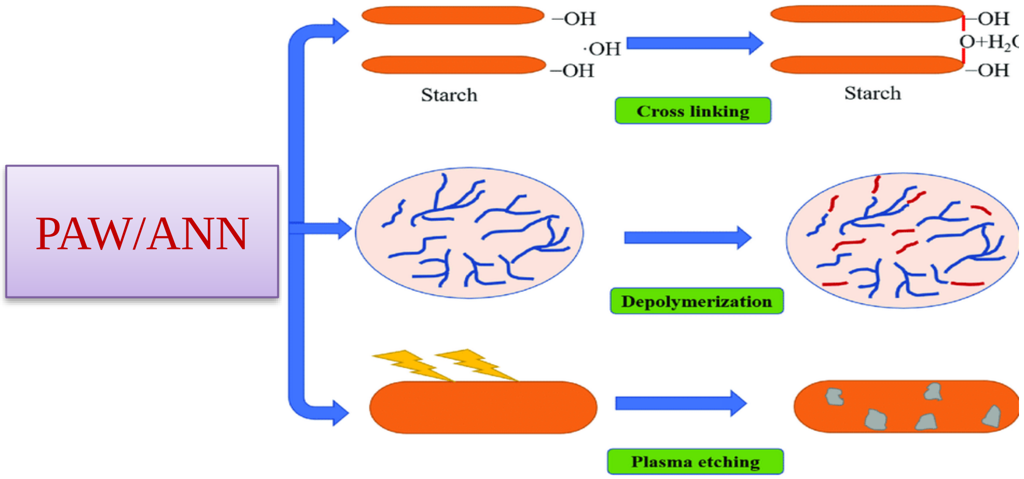
Breakdown viscosity (BDV): granule resistance to temperatures and shear rates.

Decrease ➔ higher thermal stability, higher resistance against shear exerted from high temperature and a lower deterioration tendency

Annealing with PAW treatment could improve the stability against mechanical shear and thermal stability within a short time.

Conclusions – 2

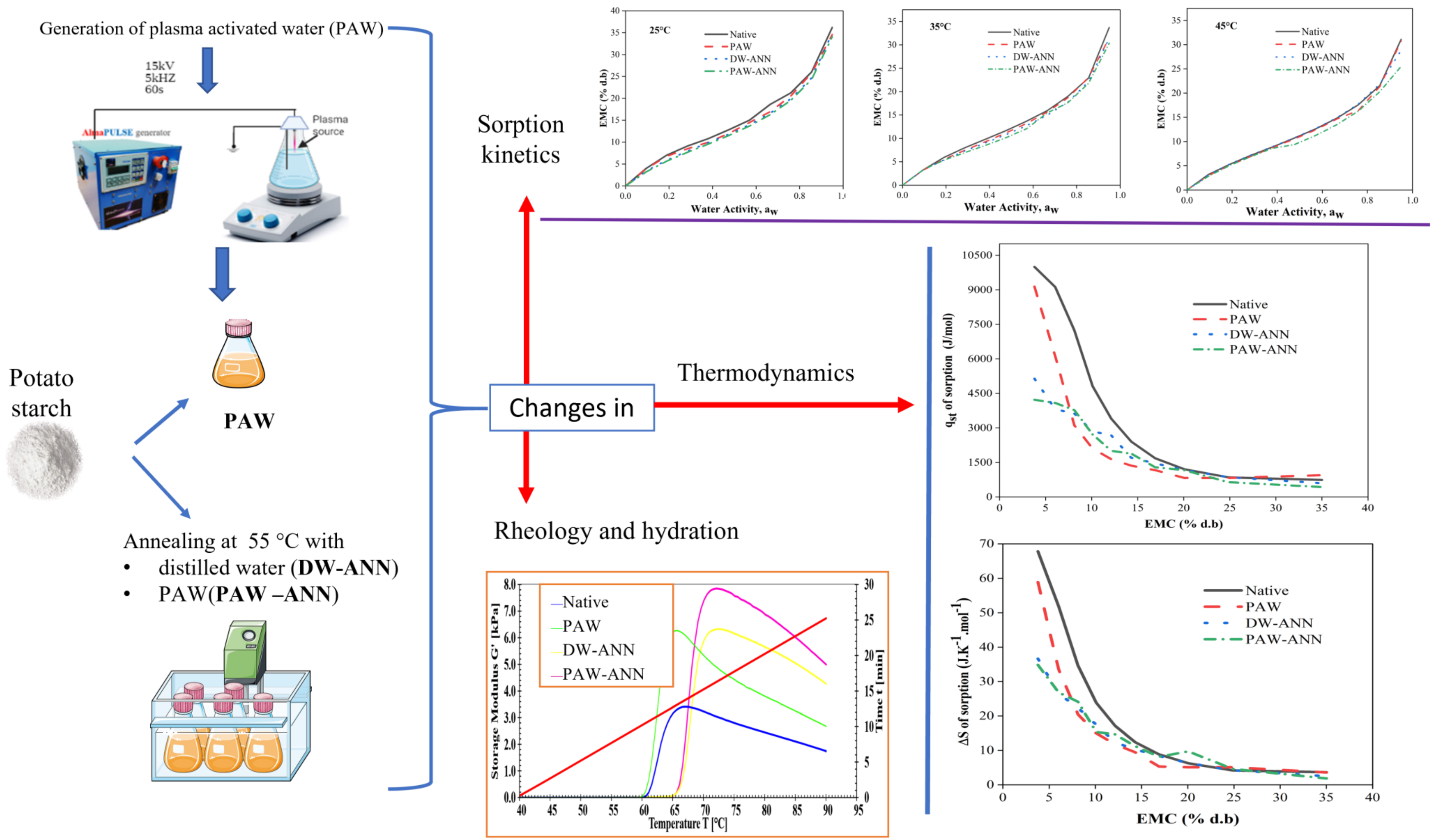
PAW+ANN ➔ synergistic effect in thermal stability and shear resistance, resulting in lower breakdown viscosity, higher elasticity and gelatinization enthalpy up to 4 h



Increased ability to better withstand high thermal and mechanical processing conditions in the food industry: use as a sustainable raw material in food applications, such as a base for baked goods, thickening agent, candies, ice cream and in processed foods

PAW-ANN combination: promising technology for the modification of starch, as environmentally friendly alternative to chemical modifications

PAW and Annealing: Effects on Sorption Isotherms, Thermodynamic and Gelatinization Kinetics of Potato Starch



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Conclusions and future work

- PAW is effective for modifying starch properties
- Effect dependent on starch type and processing parameters
- Synergistic effect with annealing

Future work should be carried out to clarify porosity (pore size), morphology, and crystallinity of the granules affected by the proposed treatments

Proteins used as ingredients

Commercially, proteins are differentiated based on:

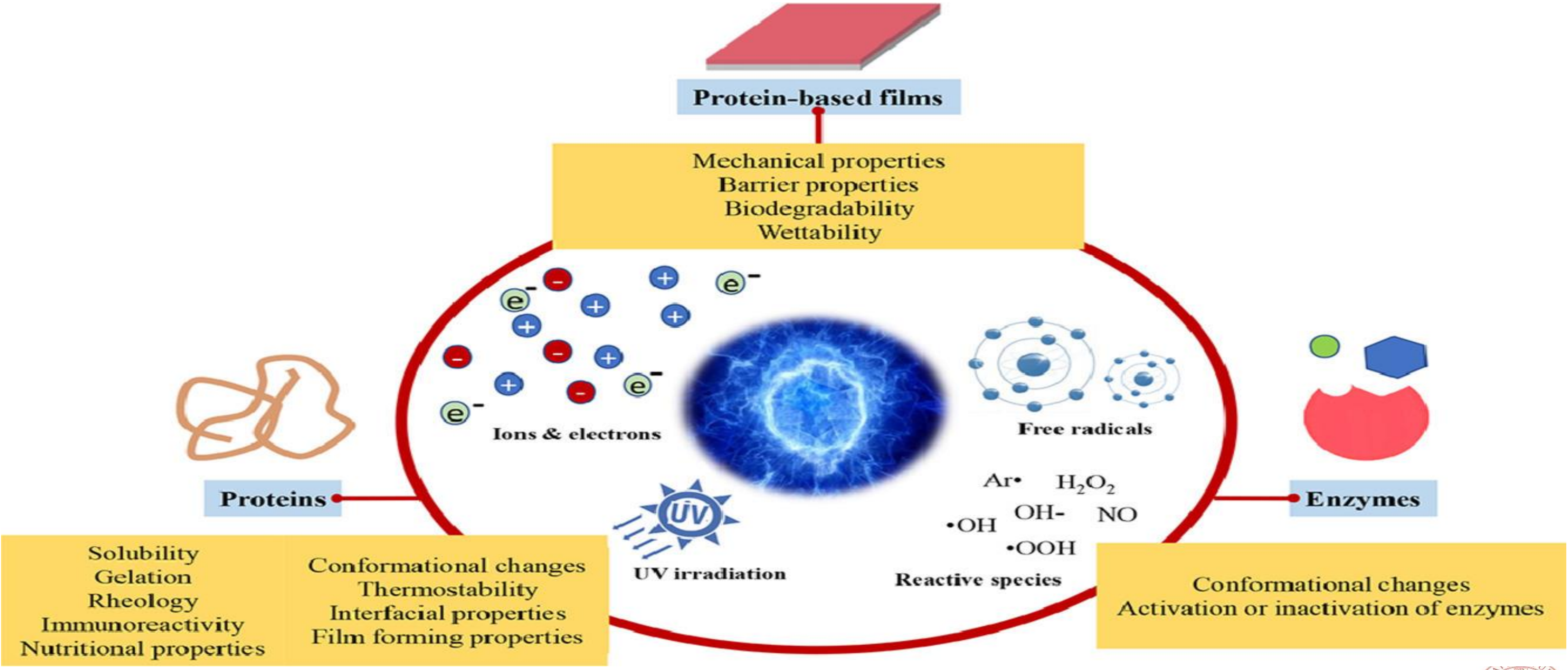
•Source: animal, insects, plants or microbes

•Protein content: flour (70-85%) concentrates (up to 85%) and isolates (higher than 85%).

Protein functionalities: ability to gel, foam, emulsify and form films and dough structure , …

Types	Form	Plant-based sources available
Flours	Powder, semolina	Soy, lupin, faba bean, pea, rice, lentil, chickpea
	Texturized (flakes, pellets)	Soy, faba beans, peas
Concentrate	Powder, semolina	Soy, lupin, faba beans, rice, lentils, chickpeas
	Texturized (flakes, pellets, crisps)	Soy, peas
Isolates	Powder	Soy, peas, rice, wheat, potato

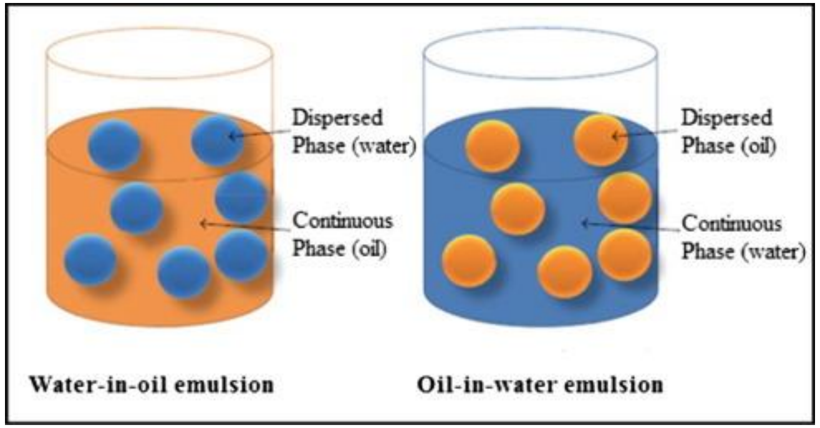
Recent trends in the application of cold plasma for the modification of plant proteins



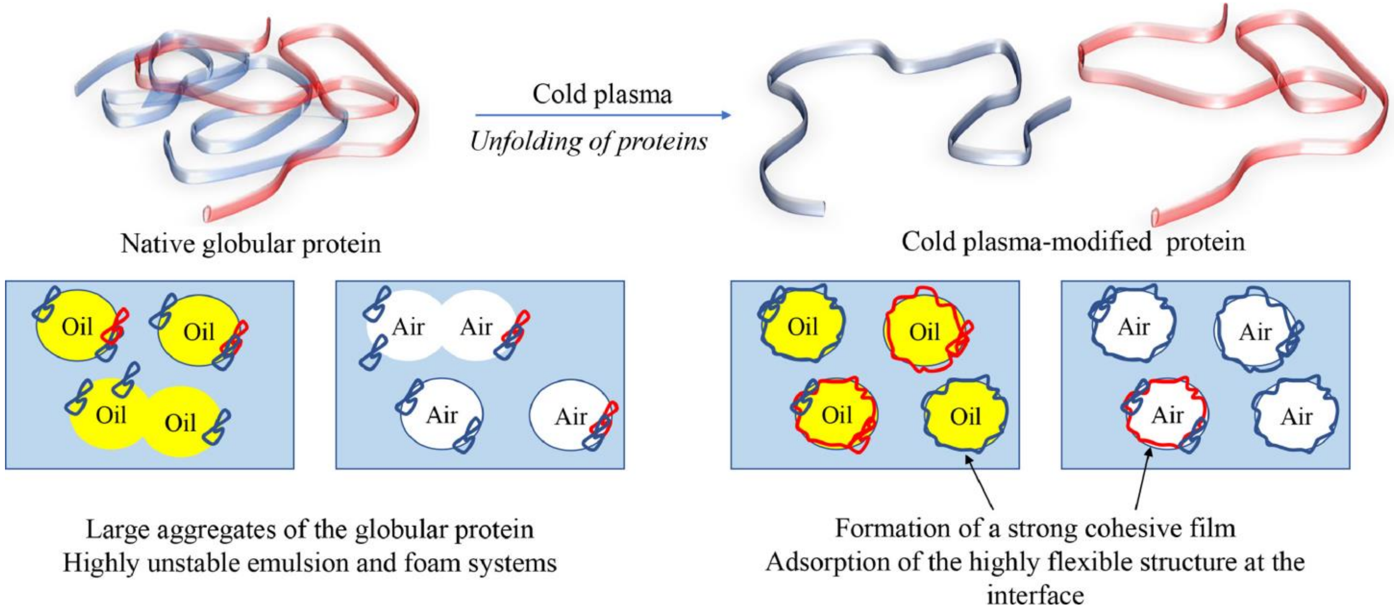
Modification of emulsifying properties

Requirements for a protein to possess good emulsifying and foaming properties:

rapid absorption at the water-air or water-oil interface, formation of a strong cohesive film at the interface by interacting with neighboring molecules



Increased protein solubility ➔ well correlated to the emulsification capacity.



Low-frequency short-term plasma ➔ more flexible structures, with the capacity to generate films at the oil-water or air-water interface.

Zhang et al., 2020

Case study: Pea Protein Isolate (PPI) Functionalization Using a Novel Cold Plasma Source: Effect of Treatment Time on Rheological Properties

Federico Drudi[a,*], Gebremedhin Gebremariam Gebremical[a], Luigi Ragni[ab], Chiara Cevoli[ab], Silvia Tappi[ab], Santina Romani[ab], Pietro Rocculi[ab], Urszula Tylewicz[ab]

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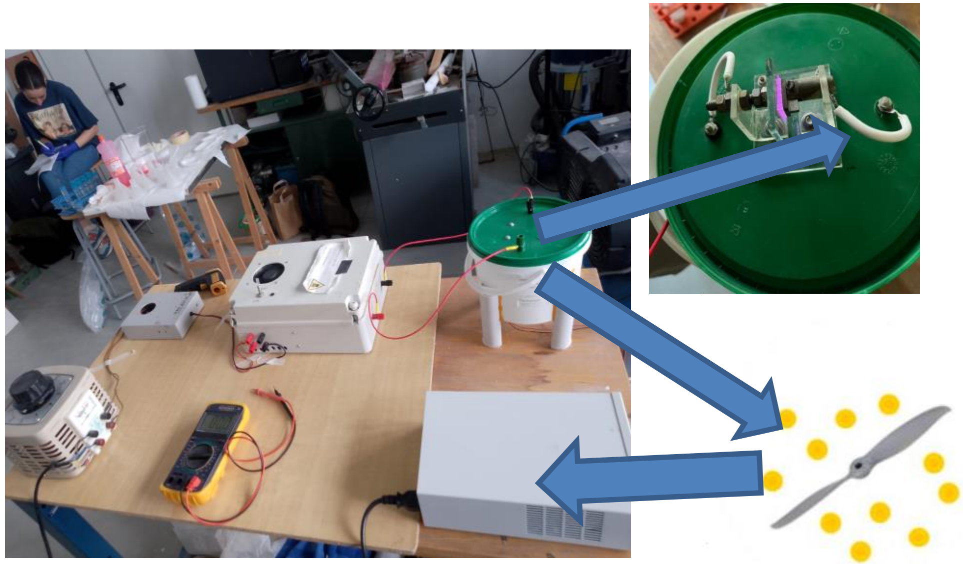
Specific objective:

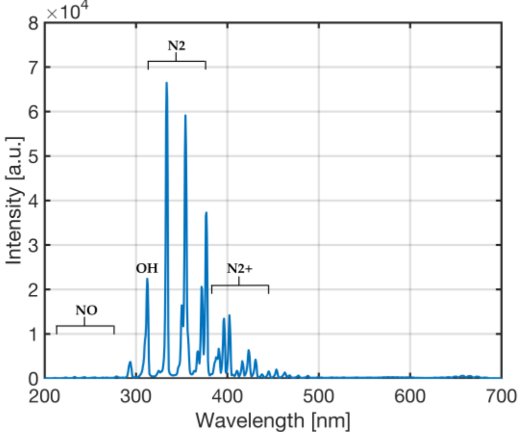
Evaluate modifications in terms of structural and rheological properties

Set up of plasma treatment

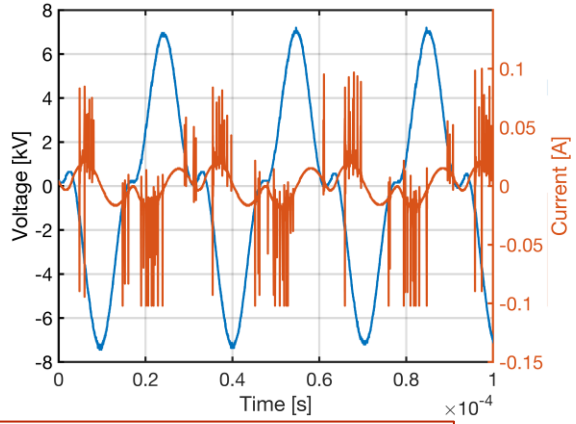


- DBD atmospheric plasma source, 20 kV 32kHz
- Fan to set in motion the powders
- Active power: 8.56 ± 0.65 W
- 1.8 cm^2 metallic electrode, 3270 cm^3 total chamber volume

Optical spectrum:



Waveform discharge:



Experimental procedure

Pea Protein Isolate
(protein content – 91%)

Treatment
5, 10, 20, 30 min
Control (untreated)

Analytical determinations
- SDS page – Primary structure
- FTIR – Seconday structure
- Solubilty
- Rheological behaviour

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Conclusions

- Plasma treatment was effective in modifying rheological properties of PPI
  → rheological results generally in agreement with other similar published works

- The improved rheological properties don't come from changes in primary structure
  → no polymerization seem to happen, in contrast with some studies

- FTIR data suggest no effect on secondary structure (minor absorbance changes on amide I and II), but:
  → FTIR spectra markedly differentiate between treatments trough PCA analysis
  → Major affected areas might be linked to protein oxidation or interaction with other non-proteinaceous components

- Tertiary structure evaluation studies (e.g. fluorescence spectra) are needed to better understand the observed rheological modifications

Concluding remarks

The investigation of cold plasma as method to modify sturcture and functionality of food components is gaining increasing interest.

It might be used to replace or to improve currently existing methods resulting in **higher efficiency and sustainability** of the process.

Investigation on mechanisms and process optimization is still required

Thank you!!

Meet the presenter

Questions?

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