FOR BETTER FOOD & HEALTH

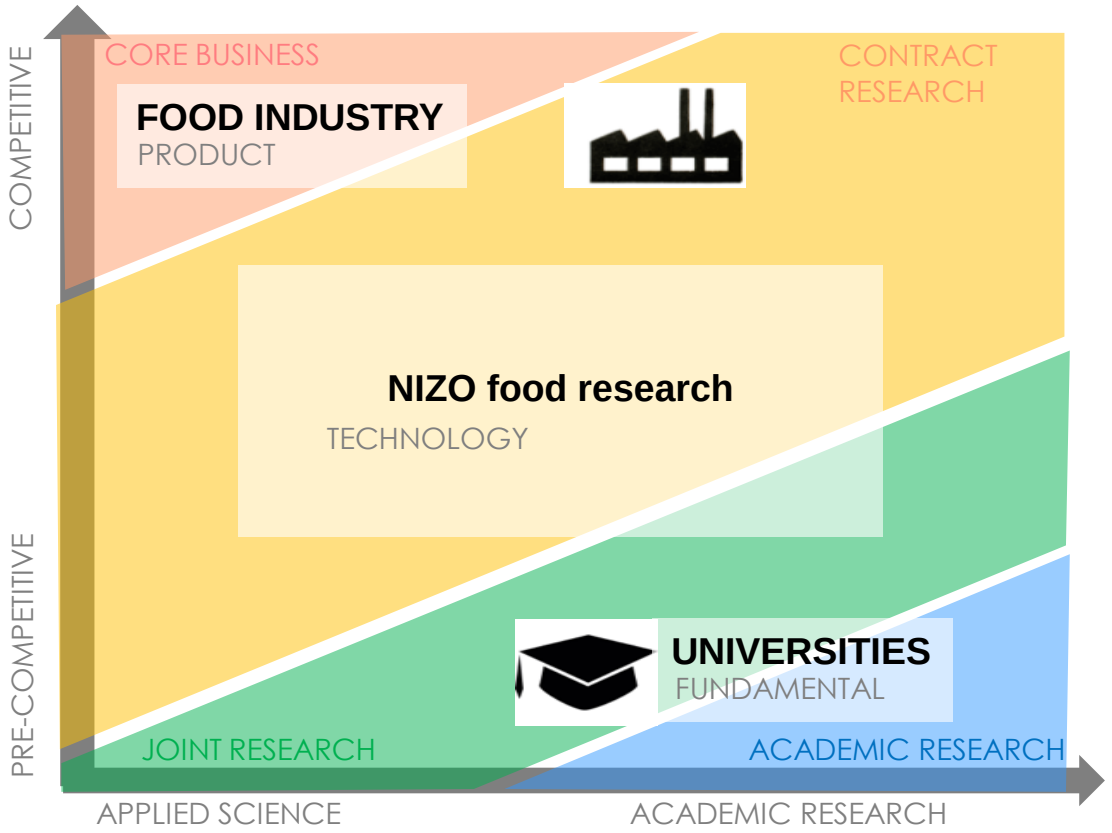
FUNCTIONALITY OF CASEIN-RICH INGREDIENTS IN NUTRITIONAL PRODUCTS: UNDERSTANDING AND OPTIMIZATION

Thom Huppertz
thom.huppertz@nizo.com

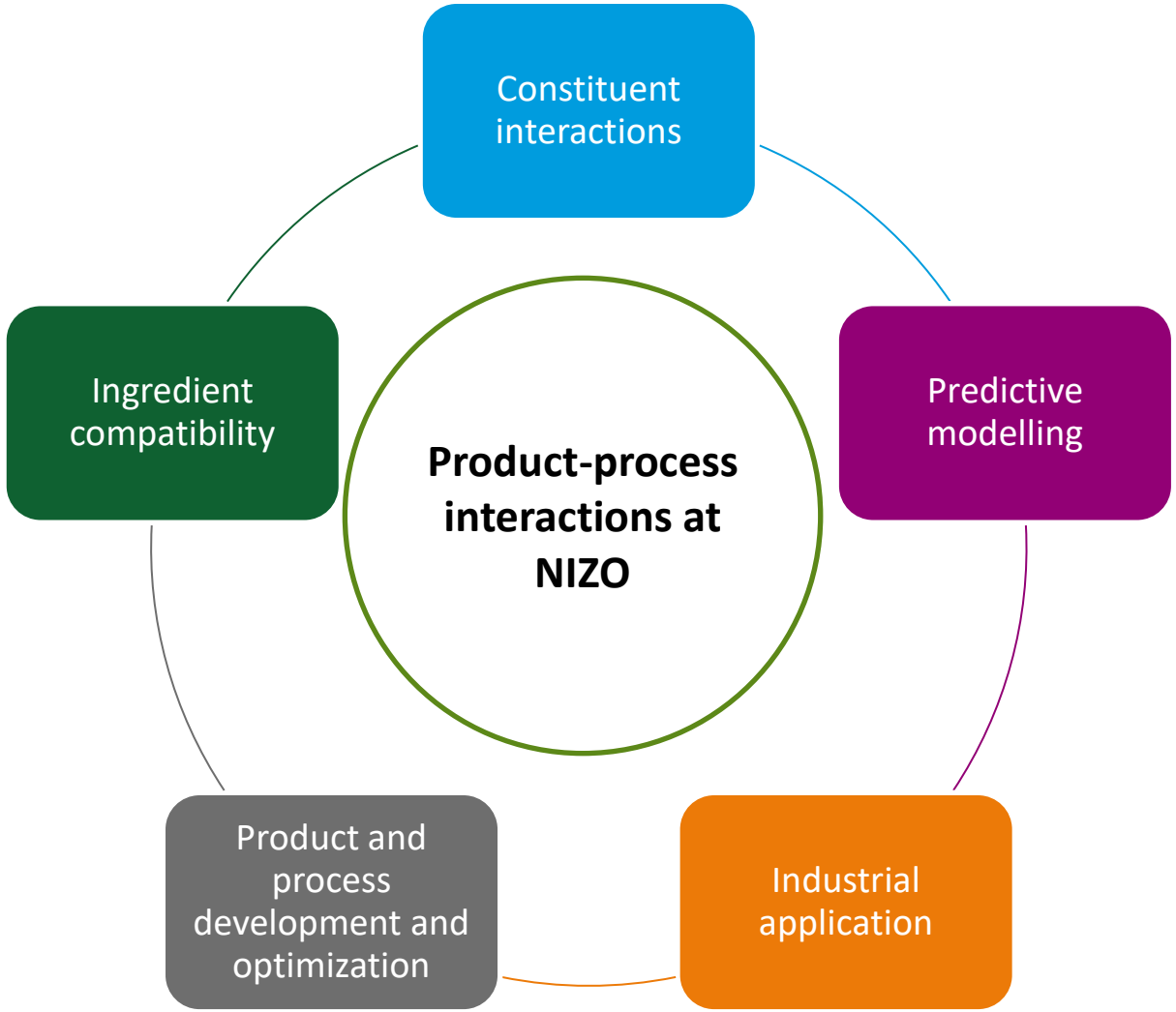
02/05/2017

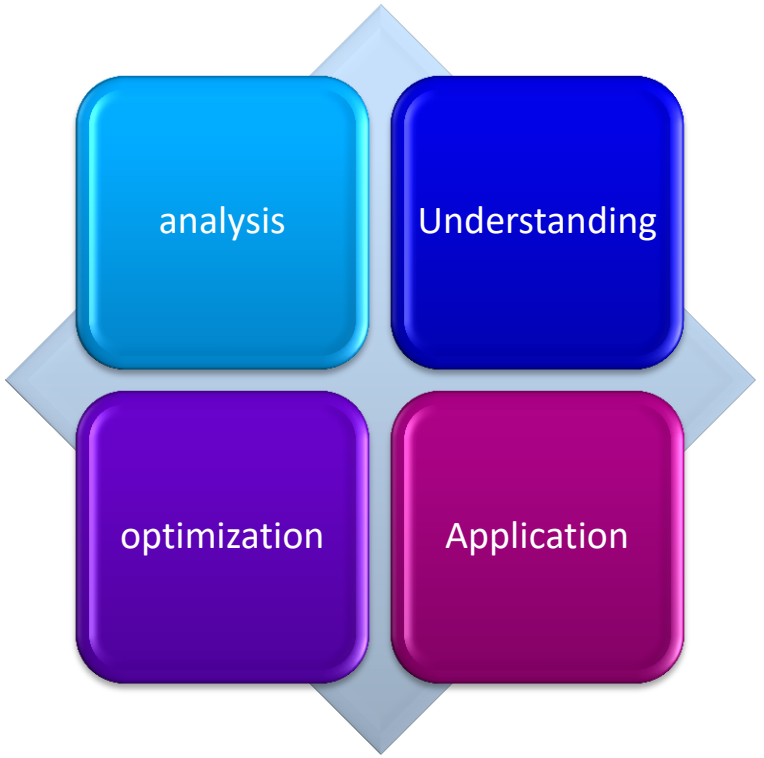
INNOVATING TOGETHER

NIZO FOOD RESEARCH: FROM SCIENCE TO SOLUTIONS

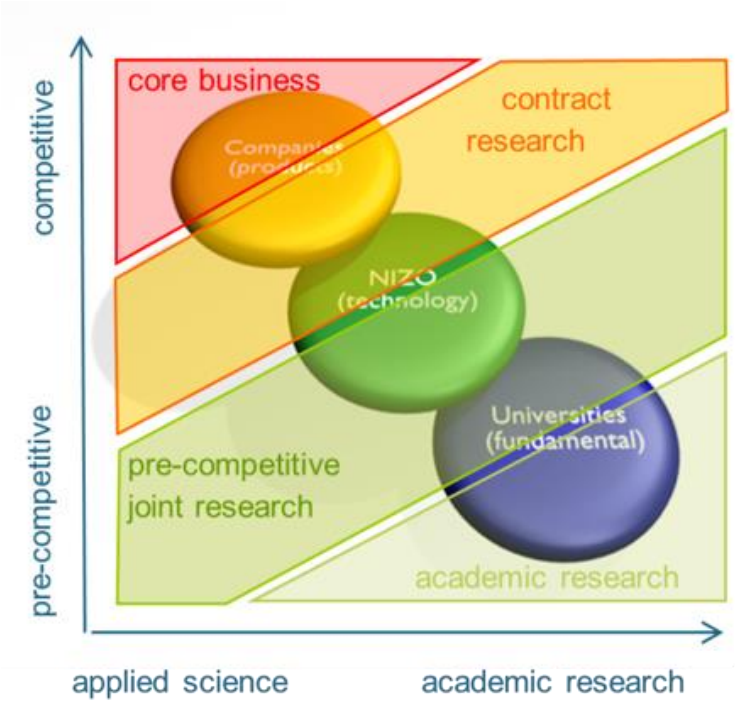


CASEIN FUNCTIONALITY IN NUTRITIONAL PRODUCTS: PRODUCT-PROCESS INTERACTIONS





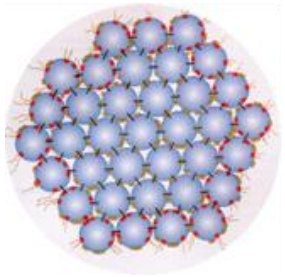
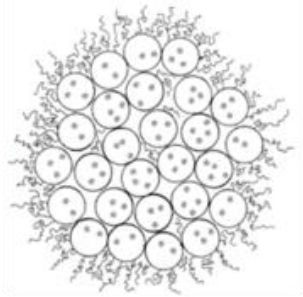
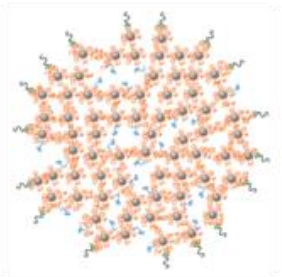
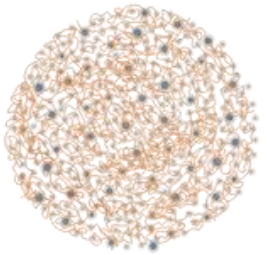
FROM SCIENCE TO SOLUTIONS: CASEIN MICELLES





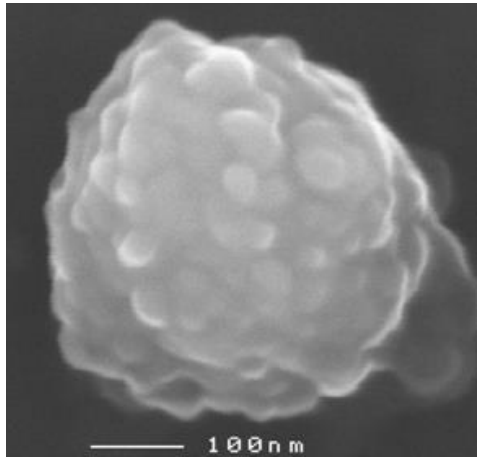


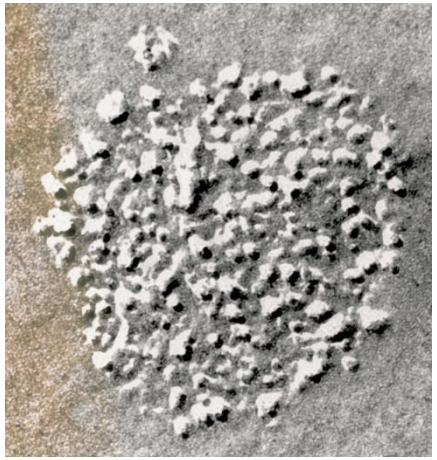
- Industial focus on functionality
- Academic focus on physical and (bio)chemical properties
- Both primarily observational and explanatory on specific conditions
- Need integrated model to predict rather than explain functionality

A TYPICAL CASEIN MICELLE

Spherical	Diameter ~200 nm	Surface structure

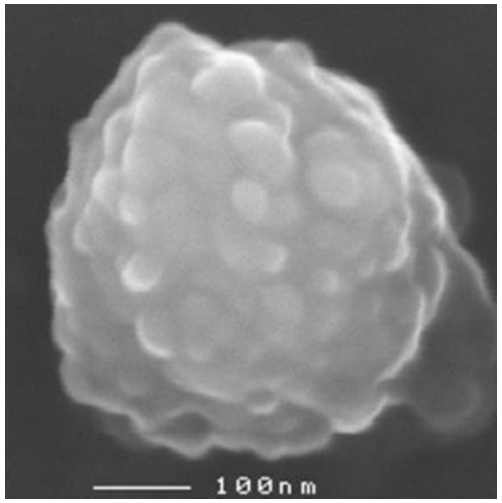


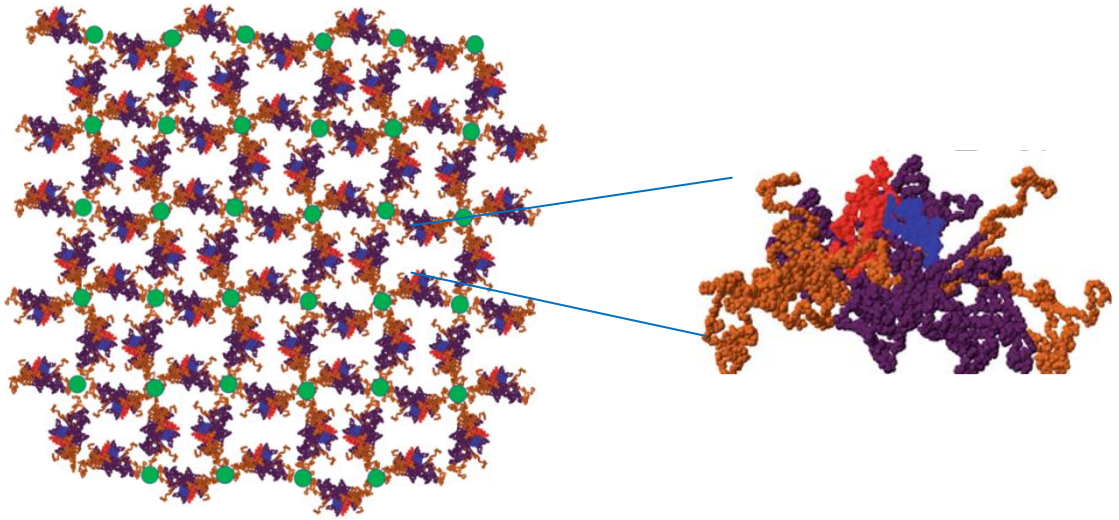


75% moisture	23.5% protein	1.5% inorganic material (primarily Ca, PO_4)

~70,000 casein molecules, 1,400,000 calcium ions and 1,000,000 phosphate ions → how to combine them to build a casein micelle

CASEIN MICELLES





- Casein micelles are a network of primary casein particles linked through calcium phosphate nanoclusters
- Inhomogeneous distribution of matter in casein micelles
- Changes in casein micelles because of:
  - Changes in casein-casein interactions
  - Changes in casein-nanocluster interactions
  - Changes in nanoclusters

CASEINS IN AN INDUSTRIAL PERSPECTIVE





The caseins are the same….

…only the concentrations and enviroment are different




THE CHANGING ENVIRONMENT

Yoghurt
High water
Low/intermediate protein
Low carbohydrate
Low pH

Protein bars
Low water
High protein
High carbohydrate
Neutral pH

Milk
High water
Low protein
Low carbohydrate
Neutral pH

Cheese
Intermediate water
High protein
Low carbohydrate
Low pH / High salt

Protein ingredients
No water
High protein
Low/high carbohydrate
Neutral pH / high salt

THE CHANGING ENVIRONMENT: NUTRITIONAL PRODUCTS

- Infant formula powders and liquids
  - Low in casein, high in whey protein
  - High fat:protein ratio
  - Fortification with minerals and minerals

- Clinical formula powders and liquids
  - High in protein
  - High in total solids
  - Fortification with minerals

- Different aspects important for powdered and liquid products

- Protein sources used are typically reconstituted powders and not liquids → is functionality maintained during ingredient manufacture?

FROM MILK TO MILK PROTEIN INGREDIENTS TO APPLICATION

- Need to understand milk proteins in milk before we can understand, control and tailor functional ingredients
- Understand the source material (milk) but also the production of the source material (physiology of lactation)

FROM MILK TO MILK PROTEIN INGREDIENT: MILK PROTEIN CONCENTRATES

- **32 commercial samples of MPC** (collected from Europe, North & South America, Oceania)

Samples compared on basis of:

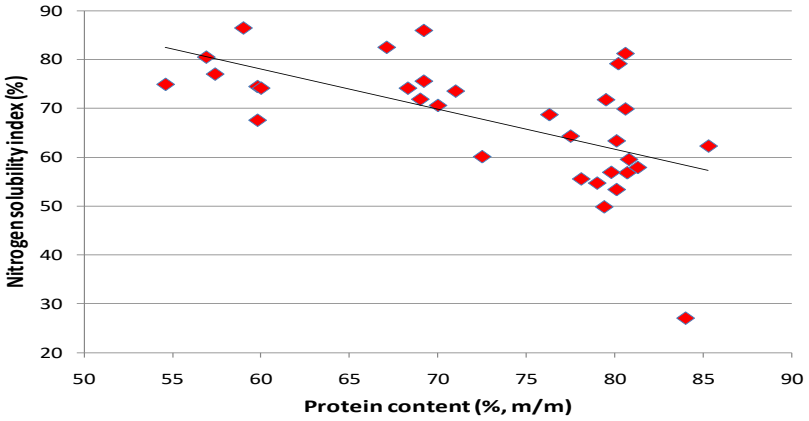
- Composition (gross composition, minerals, amino acids)
- Solubility (following 0, 6 and 12 months storage at 20°C)
- Powder properties (bulk density, particle size, dispersibility)
- Physicochemical properties (denaturation, lactosylation, pH)
- Functional properties (emulsification, foaming, gelation, heat stability, viscosity)

55	Protein (%, m/m)	85
3.5	Moisture (%, m/m)	6.6
14	Calcium (mg/g)	24
0.3	Sodium (mg/g)	14
17	Lactosylated β-lactogl. (%)	83
20	Denatured β-lactoglobulin (%)	80
38	Dispersibility (%)	100
27	Nitrogen solubility index (%)	87
0	Heat stability (min)	42
15	Gel strength (g)	266
178	Foam overrun (%)	390

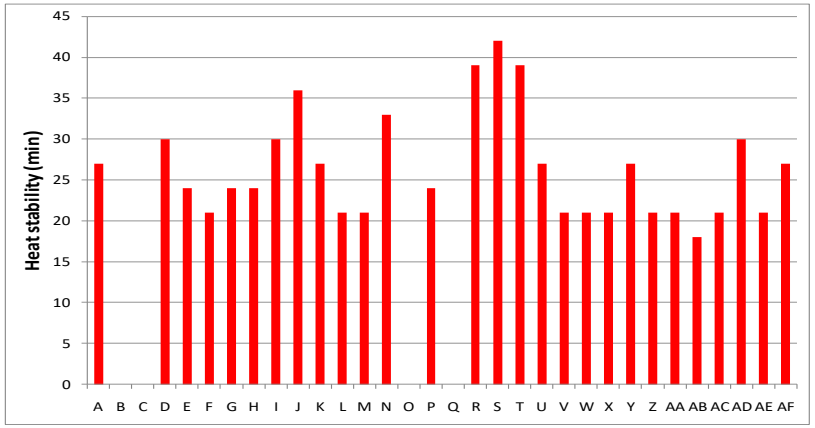
MILK PROTEIN INGREDIENTS: THE DIFFERENCES

- Comparison of these commercial samples reveals strong differences between products:

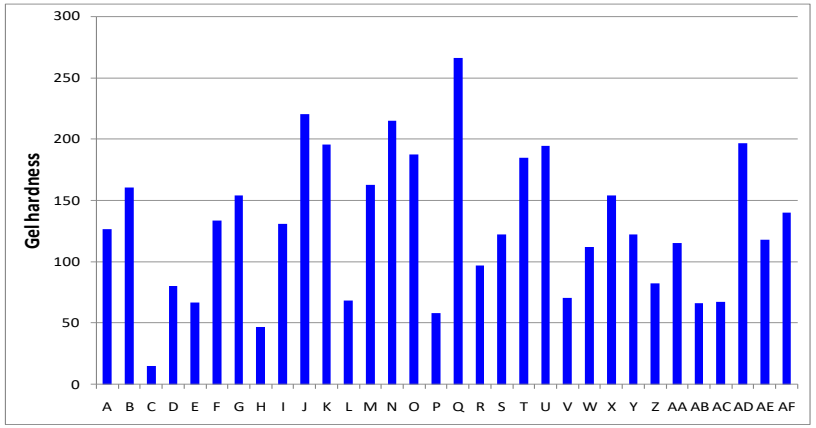
Solubility



Heat stability



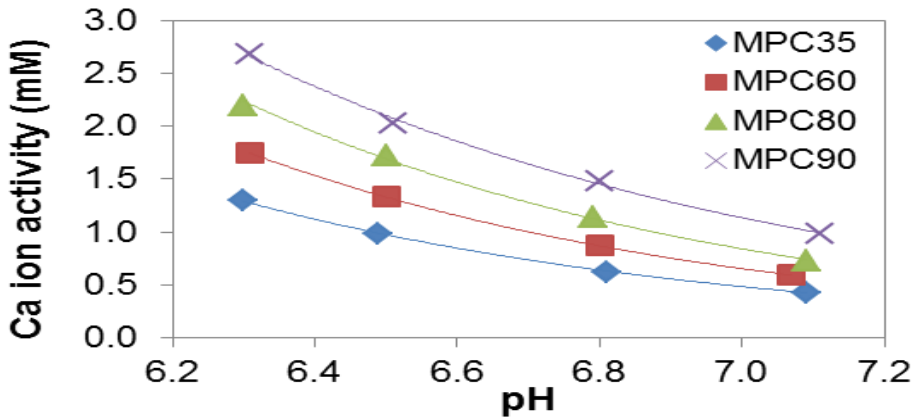
Gelation

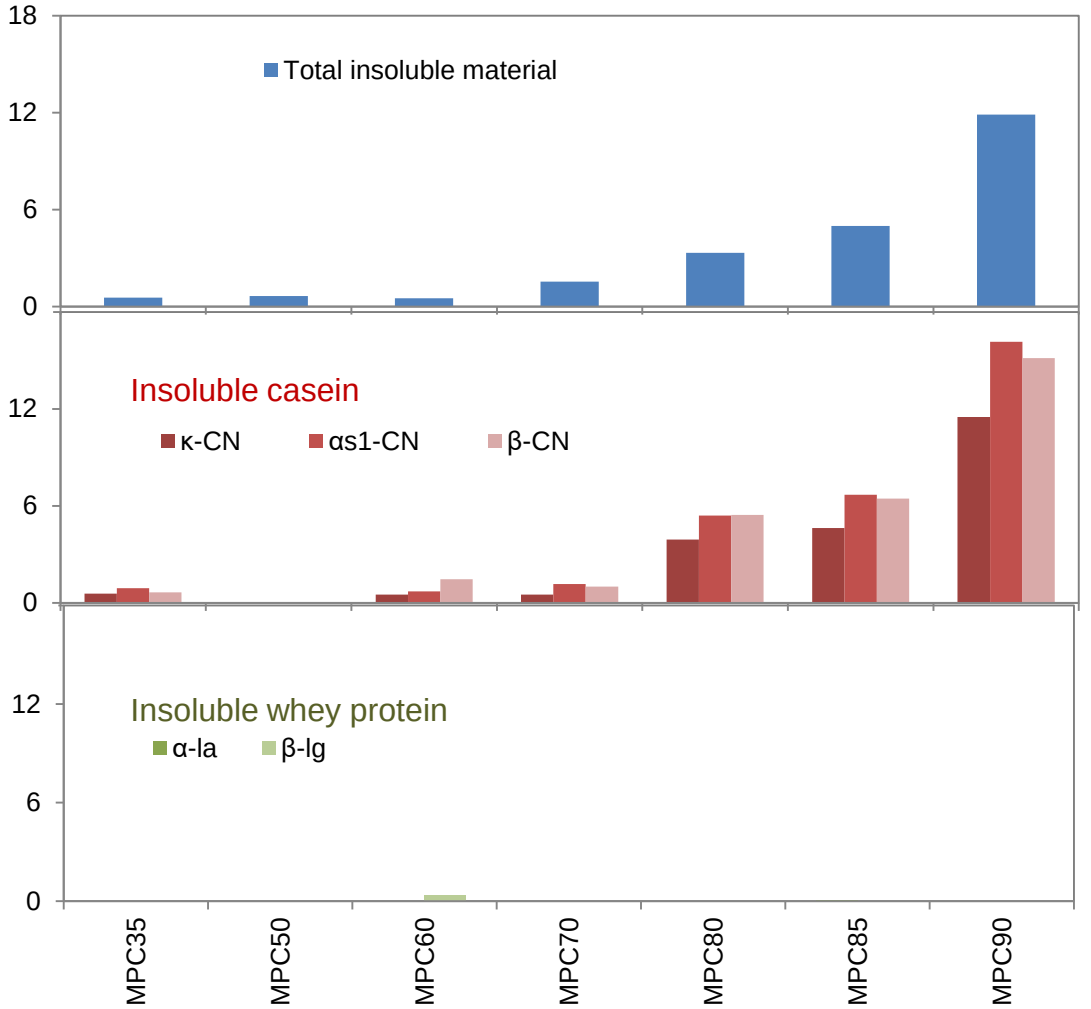


- Variation is not correlated to differences in composition
- Processing conditions were unknown

- **How can these differences be explained?**

SOLVING THE PROBLEMS: INSOLUBILITY DEVELOPMENT DURING DRYING





- 100% solubility of MPC up to 70% protein immediately after drying
- Reductions in solubility during drying in MPC80-MPC90
- Reduced solubility solely related to casein; whey proteins remain fully soluble!
- Combination of high casein concentration, high temperature and high a$[Ca]^{2+}$ results in casein micelle aggregation

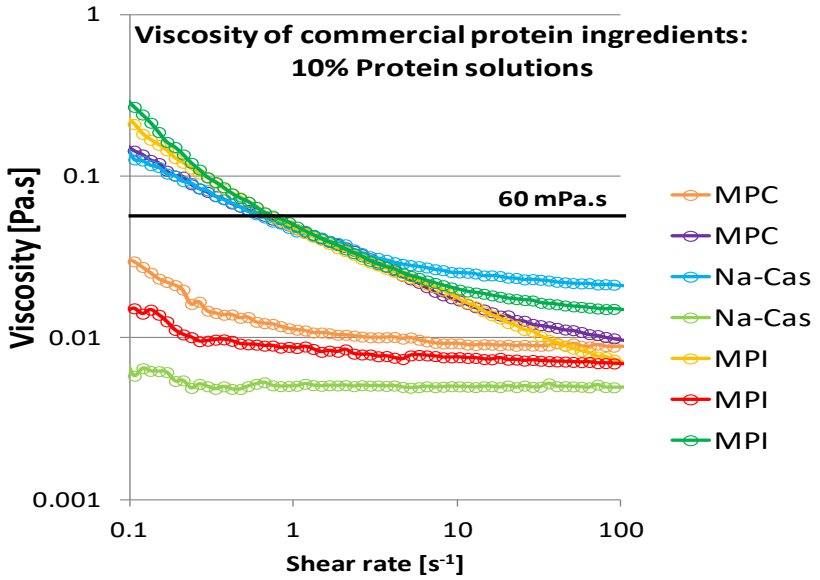
HIGH PROTEIN DRINKS

Product composition

- 10% protein
- 10% fat
- 30% carbohydrate
- ~3% minerals/vitamins/etc

Product properties

- Viscosity: 50-100 mPa.s (yoghurt-drink)
- Shelf-stable for 6-12 months
- No compromise on flavour/mouthfeel etc

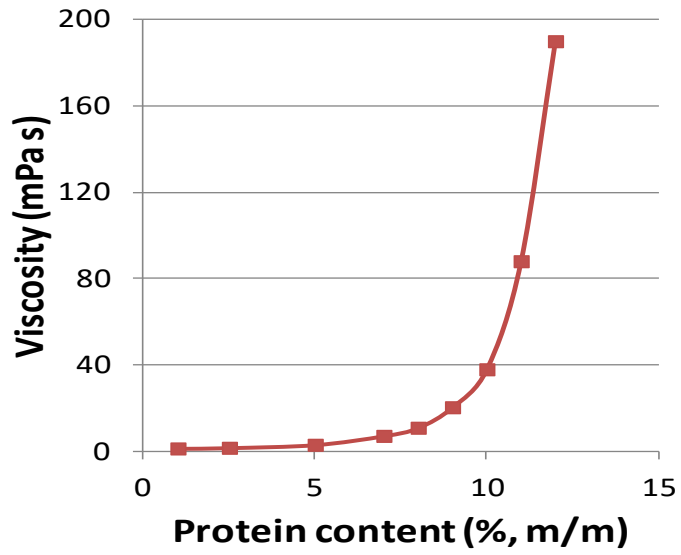


Typical process

- Recombination of dry ingredients
- Homogenization
- UHT treatment and aseptic filling

Challenges on the protein ingredient:

-Low viscosity
-Good emulsification
-Excellent heat stability
-No flavor



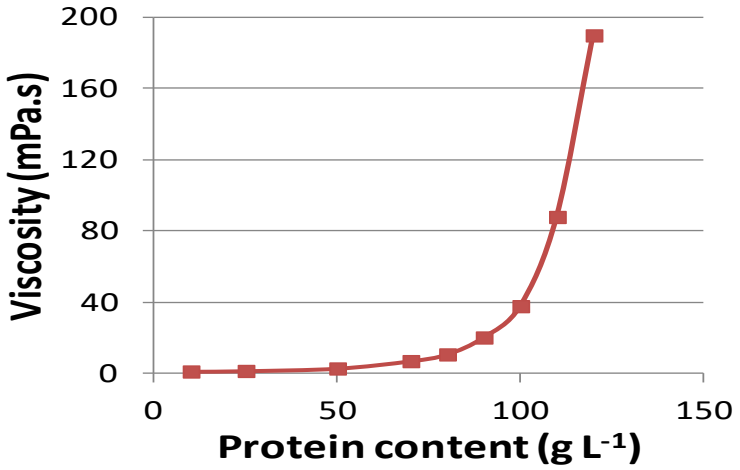
PROTEIN INGREDIENTS FOR HIGH PROTEIN DRINKS

	Viscosity	Emulsification	Heat stability
MPC/MPI	Medium	Good	Medium/High
Na-caseinate	High	Good	High
Ca-caseinate	Low	Good	Medium
WPC/WPI	Low	Good	Low

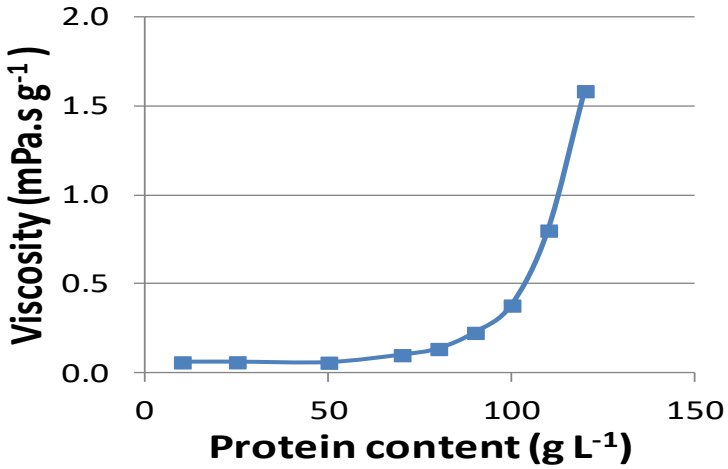
- Combination of low-viscosity with high heat stability not available in traditional range of ingredients
- Ingredients need to be optimized for application in high protein-drinks:
  - Increased heat stability of calcium caseinate / whey protein ingredients
  - Reduced viscosity of sodium caseinate

LOW-VISCOUS HEAT-STABLE CASEINATE

Viscosity of sodium caseinate



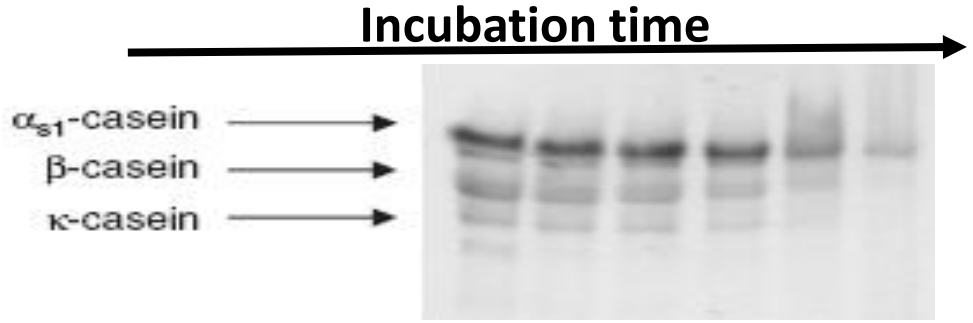
Viscosity of sodium caseinate corrected for protein content

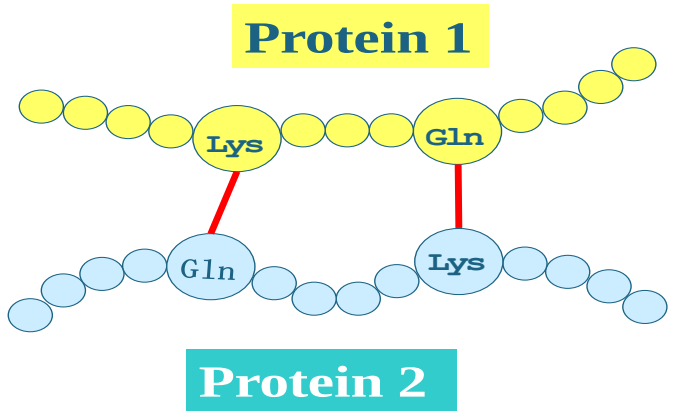


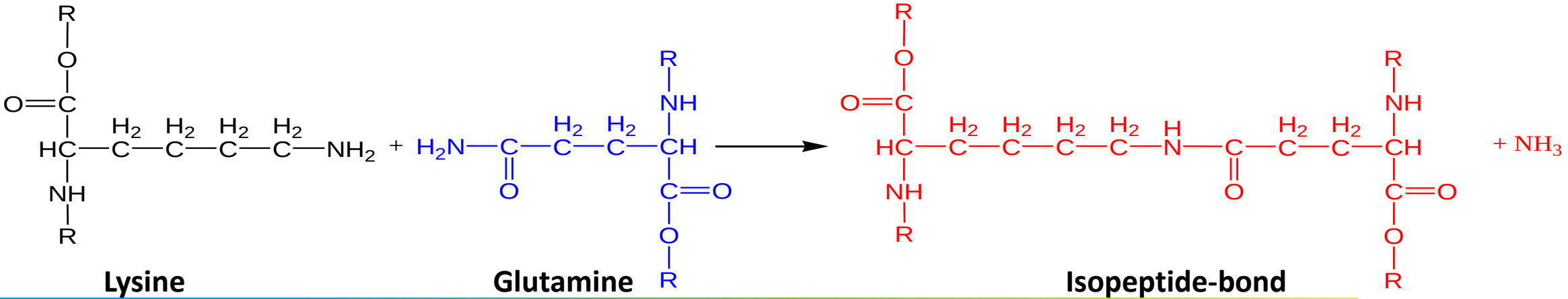
- Protein-corrected viscosity remains constant up to ~50 g L^{-1} → dispersion of protein particles
- Protein-corrected viscosity increases strongly >50 g L^{-1} → polymer solution / network
- Can caseinate structures at low concentration be stabilized to preserved viscosity at high concentration ?

ENZYMATIC CROSS-LINKING OF CASEINS

- Transglutaminase (TGase) catalyzes formation of covalent iso-peptide bond between lysine and glutamine
- Caseins excellent substrates for TGase
- Effect on functionality of:
  - Casein micelles
  - Caseinates





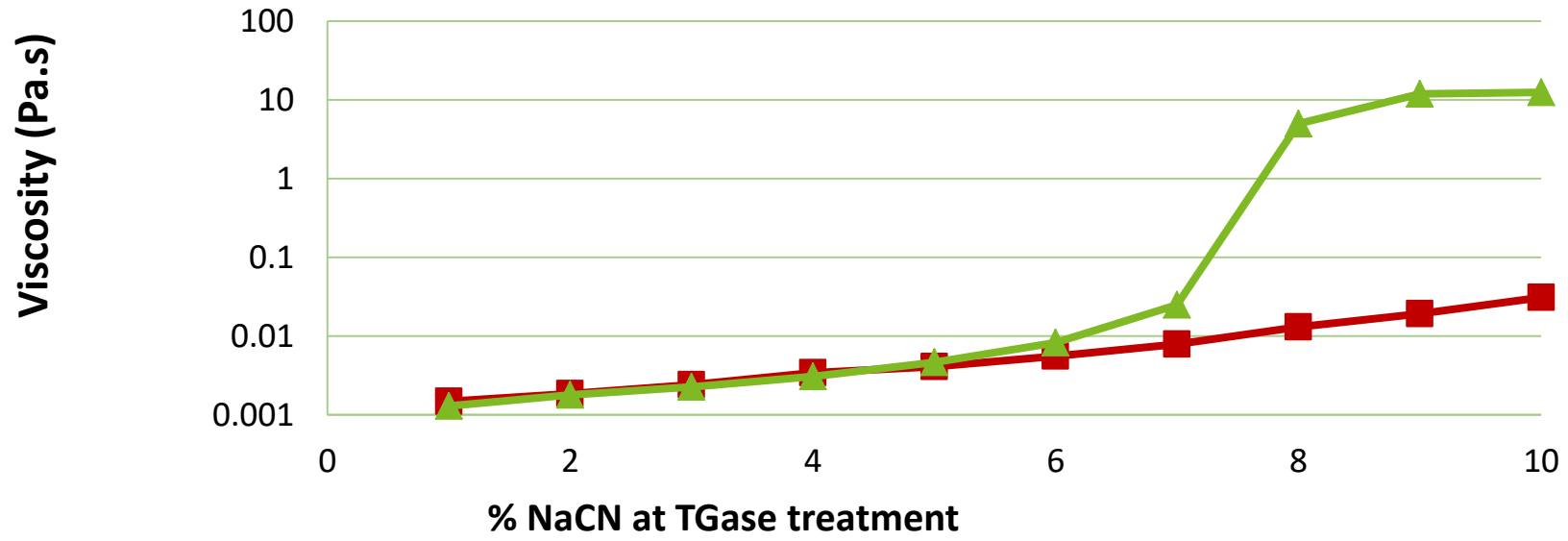


Lysine Glutamine Isopeptide-bond

VISCOSITY OF TGASE-TREATED SODIUM CASEINATE

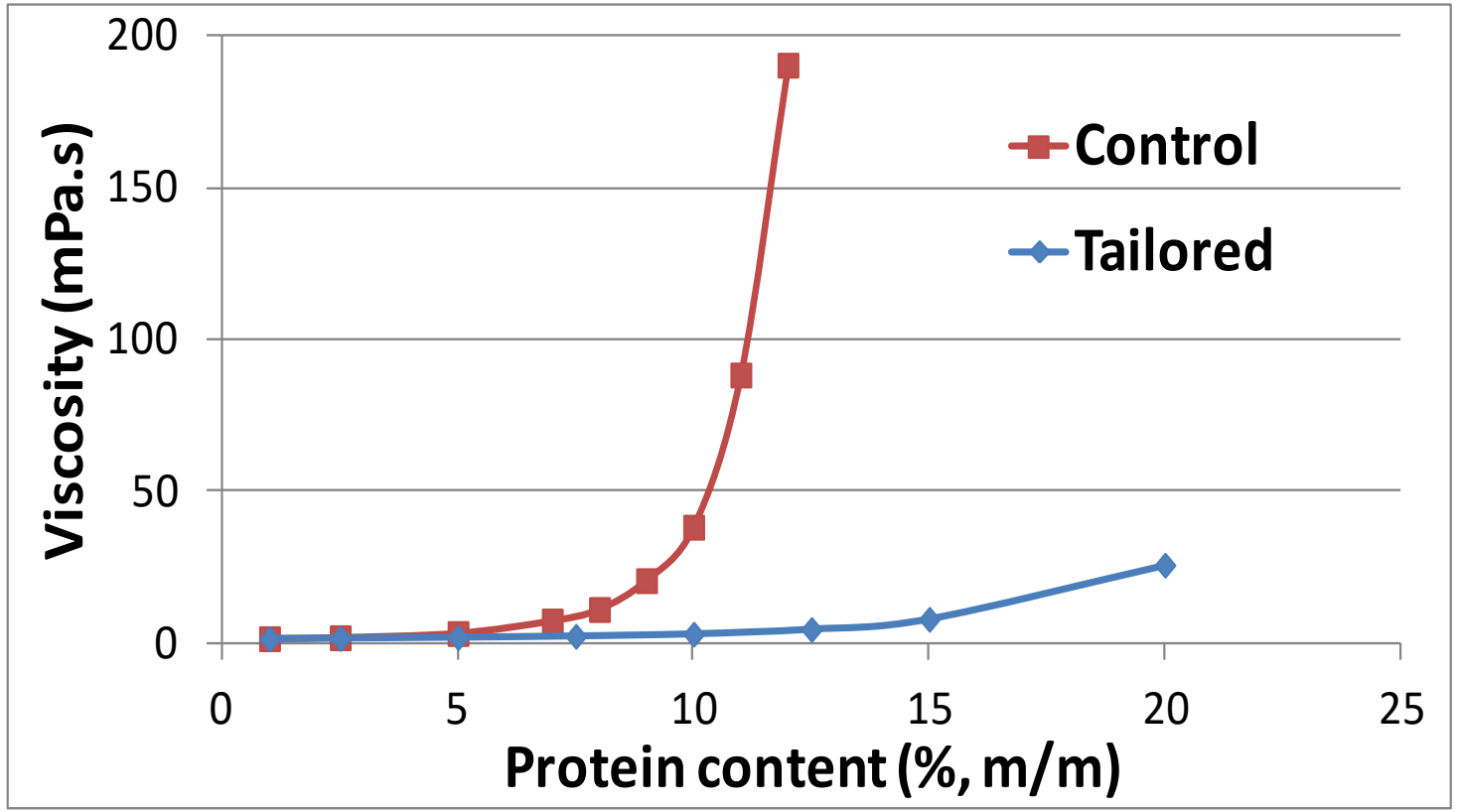
TGase-treated NaCN suspensions

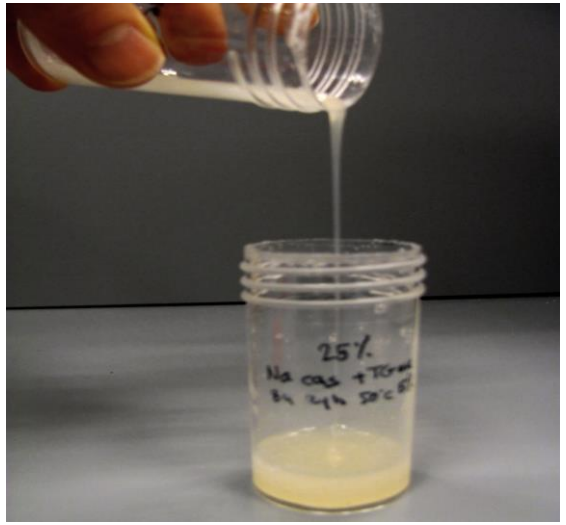
Red = untreated / Green = TGase-treated



- Complete cross-linking of casein in all cases
- <6% sodium caseinate → little effect of TGase treatment on viscosity
- >6% sodium caseinate → strong increase in viscosity → possible use as viscosifying agents

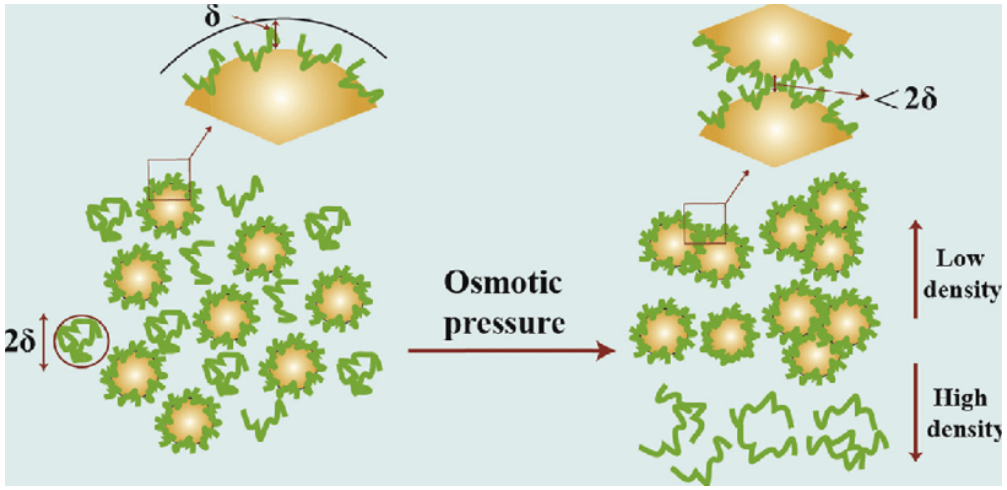
CROSS-LINKED CASEINATE

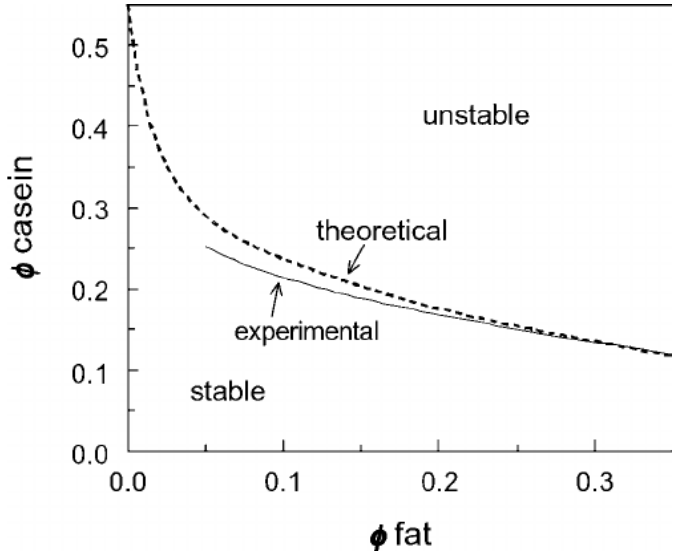


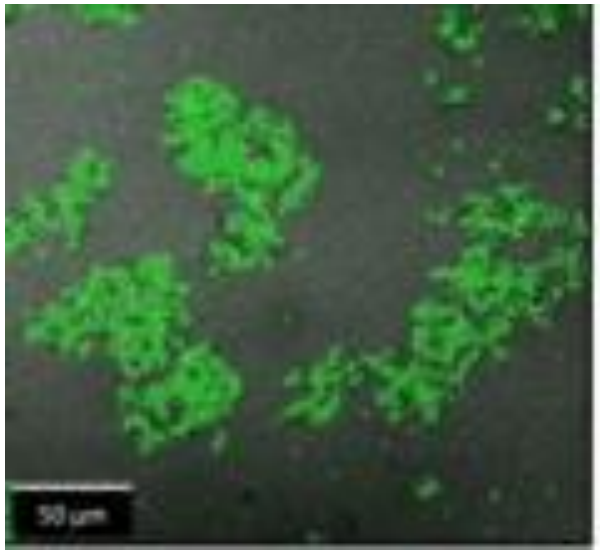


EMULSION STABILITY IN HIGH PROTEIN DRINKS

- ‘traditional ‘ creaming limited in high protein drinks due to low particle size and high viscosity
- At high volume fractions of protein particles and emulsion droplets, depletion flocclation become a driver for clustering of emulsion droplets and resultant creaming
- Control of particle sizes of emulsion droplets and protein particles crucial

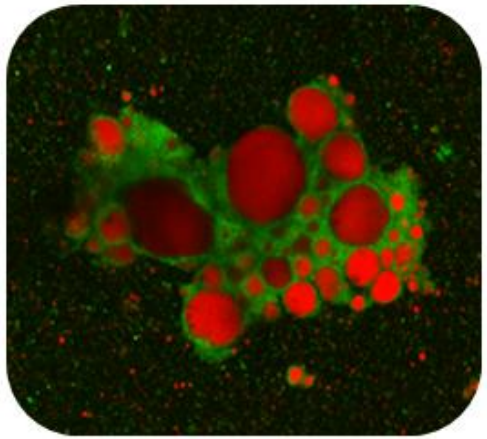






INGREDIENT COMPATIBILITY: STABILITY OF INFANT FORMULA

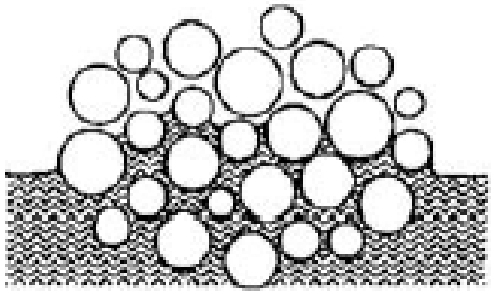
- Infant formula:
  - Typically contains both milk powder and WPC as ingredients
  - Heat-load during infant formula manufacture can result in protein instability, leading to:
    - Insolubility
    - White flecks



RECONSTITUTION OF POWDERS

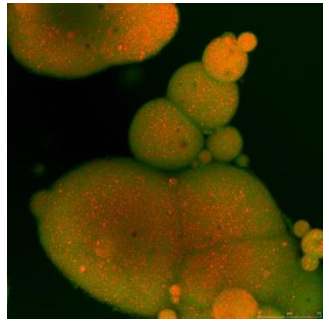
Wettability

- Particle level:
  - Surface composition
  - Wetting angle



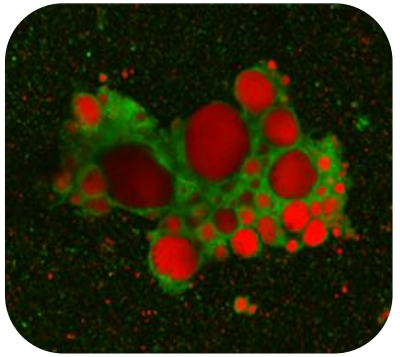
Dispersibility

- Bulk level:
  - Capillary displacement
  - Particle size distribution
  - Pore size between particles
  - Capillary contraction



Solubility

- Molecular level:
  - Fat
  - Protein
  - Carbohydrate

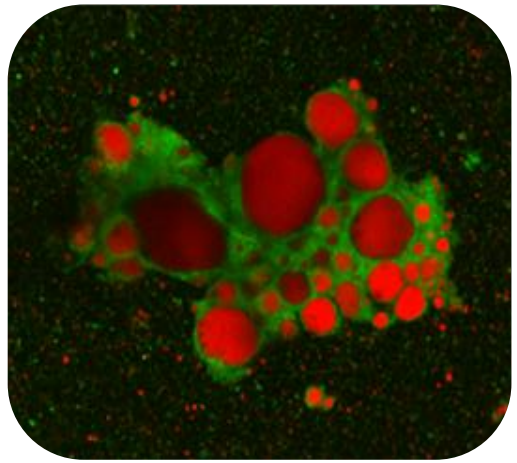


INSOLUBILITY DEVELOPMENT

Thermal stability of skim milk concentrate/powder[a]

Moisture content (%)	ISi_0 (ml)	T (°C)	$t_{ISi=0.3}$ (s)
3	<0.05	70	1.8×10^5
7	<0.05	70	1.1×10^4
3	<0.05	100	1200
7	<0.05	100	720
9	<0.05	95	20
12	<0.05	95	<7
14	8.5	–	–
25	9.0	–	–
35	<0.05	–	–
40	<0.05	–	–
50	<0.05	85	275
50	<0.05	95	50

[a] ISi_0 = insolubility index before heat treatment; $t_{ISi=0.3}$ = heat-holding time needed to increase ISi to a value of 0.3 ml.

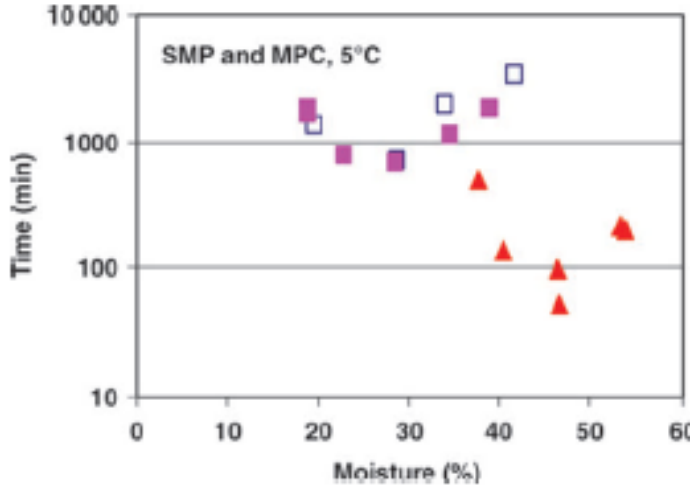


- Rapid insolubility development between 70 and 90% dry matter
- Protein aggregation as combination of:
  - High temperature
  - High protein
  - Low pH
  - High ionic strength
- In spray-dried emulsions, insolubility mas also show as aggregation of protein-stabilized emulsion droplets

INSOLUBILITY DEVELOPMENT: WHEN DOES IT HAPPEN

Moisture content (%)	$t_{ISi-0.3}$ (s)
3	1.8×10^5
7	1.1×10^4
3	1200
7	720
9	20
12	<7
14	–
25	–
35	–
40	–
50	275
50	50

Time to reach 0.3 mL insolubility in SMP at different temperatures

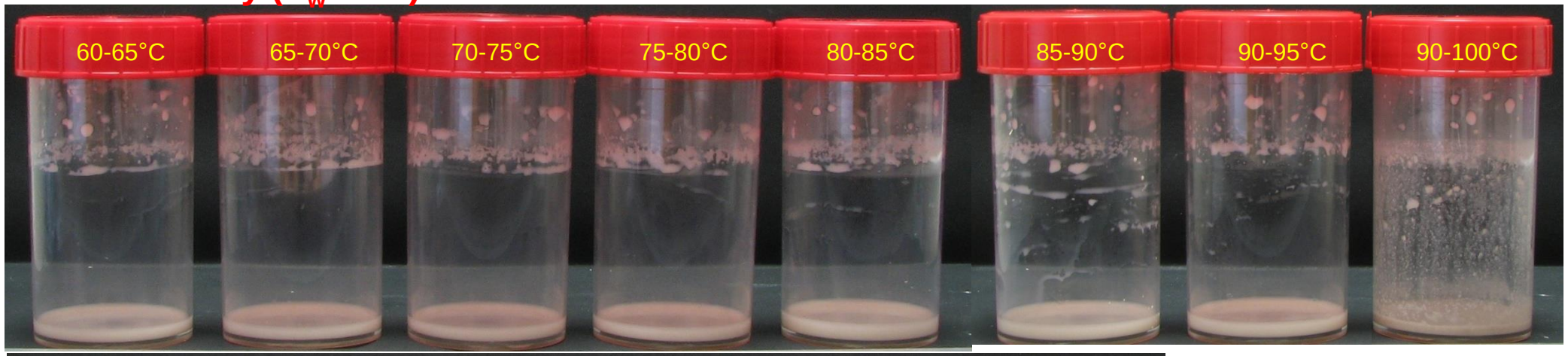


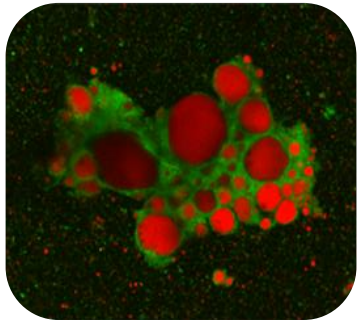
Time to reach 6 mL insolubility at 5°C for SMP (□,■) and MPC70 (▲)

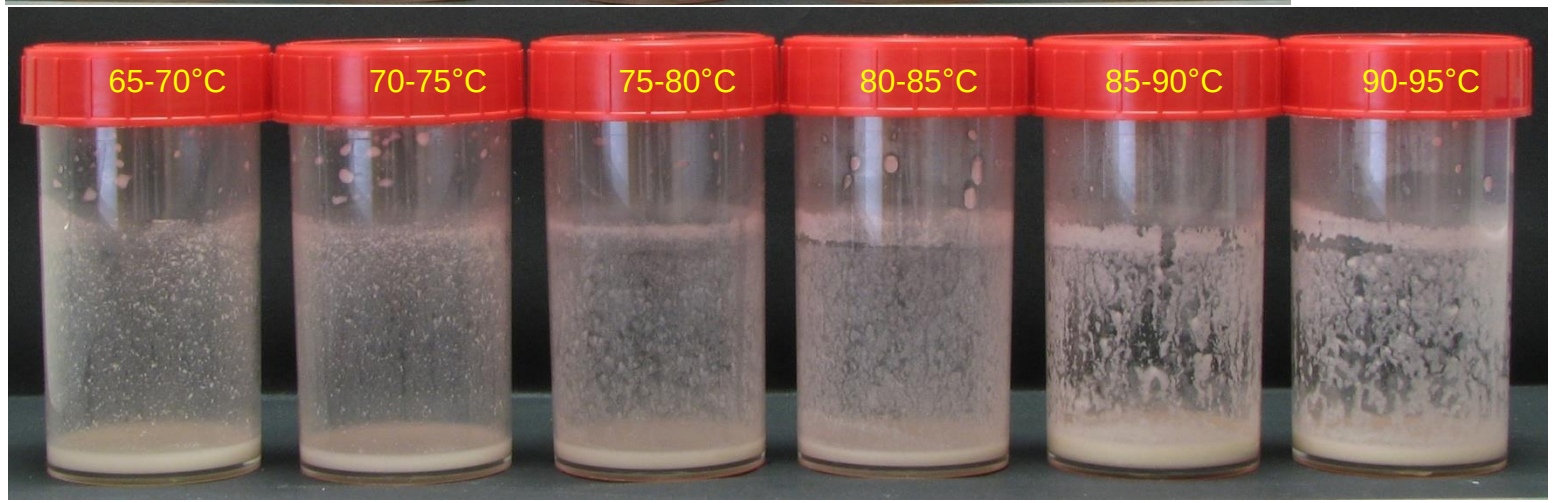
- Rapid insolubility development between 70 and 90% dry matter for SMP and 45 – 60% dry matter for MPC70, i.e., at ~25-35% protein → in the drying chamber
- Protein aggregation as combination of high temperature, high protein content, low pH, high ionic strength
- Contributory factors to insolubility the same as for heat stability
- At even higher solids content mobility sufficiently restricted to reduce/prevent aggregation

INSOLUBILITY: INDUCING EMULSION INSTABILITY

Heated dry (A_w ~0.2)







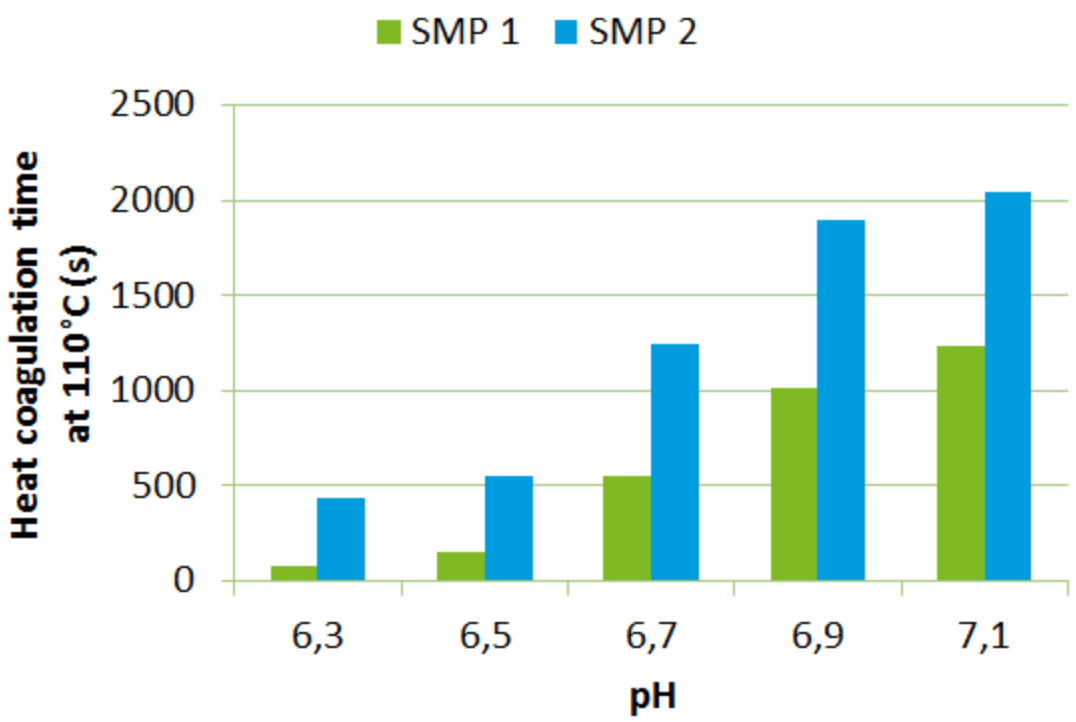
Heated wet (A_w ~0.35)

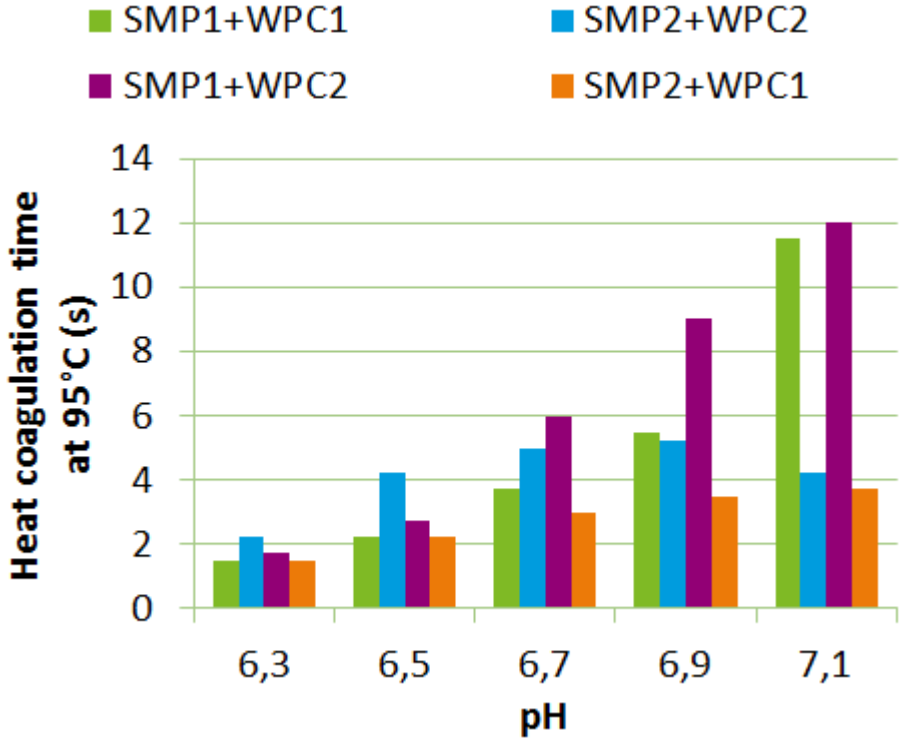
- Fleck formation largely caused by heat-induced emulsion destabilization
- Main contributors:
  - Heat stability of formulation
  - Heat-load during processing
    - Temperatures
    - Particle size

INGREDIENT COMPATIBILITY: STABILITY OF INFANT FORMULA

- Skim milk powder
  - Skim milk powder 1: ~50% whey protein denaturation (medium-heat)
  - Skim milk powder 2: ~95% whey protein denaturation (high-heat)
- Whey protein concentrate
  - Whey protein concentrate 1: ~20% whey protein denaturation
  - Whey protein concentrate 2: ~50% whey protein denaturation
- Behavior of blends vs. individual ingredients in relation to heat stability

INGREDIENT COMPATIBILITY: STABILITY OF INFANT FORMULA

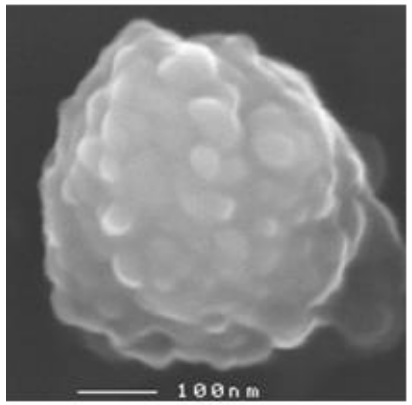




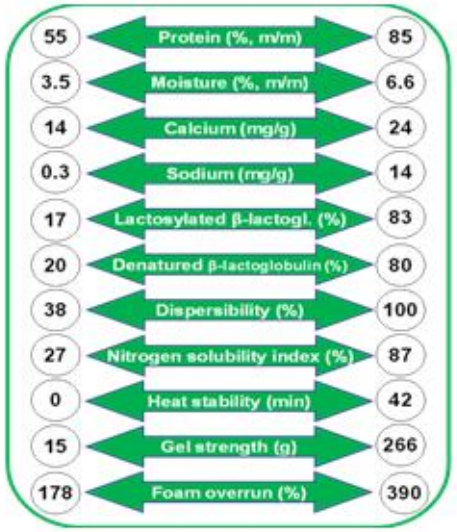
- Heat stable SMP works does not give highest stability in combination with WPC
- Test in appropriate systems when selecting ingredients
- Combine ingredient functionality with ingredient compatibility

Casein functionality for nutritional products: from science to solutions

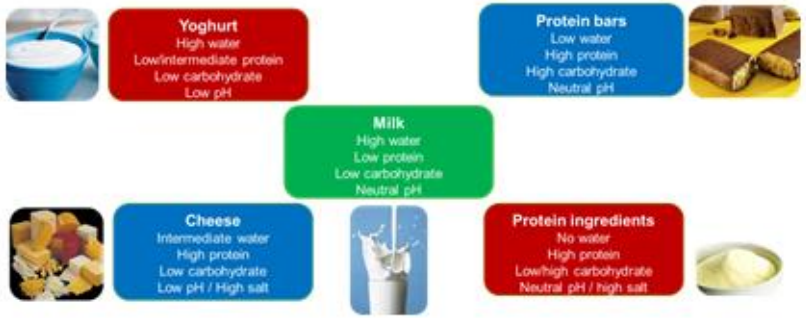
Fundamentals



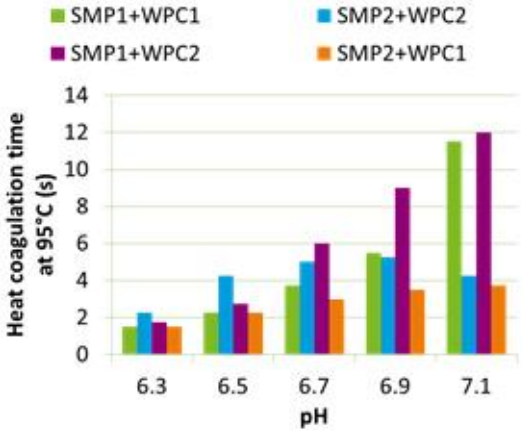
Changes during processing



Environment for application



Compatibility



Characterization → Understanding → Optimization → Application

INNOVATING TOGETHER

www.nizo.com