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Technological aspects associated with the development of food with specific nutritional properties

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CIDCA - La Plata

Province of Buenos Aires. ARGENTINA

The staff of 150 members is integrated by an interdisciplinary research group specialized in:

- food processing,
 - food preservation,
 - food engineering,
- covering different areas:
chemistry, biochemistry,
biology, microbiology
toxicology and
engineering.



The objective of this presentation is to analyze results obtained in different research works, about the technological aspects, related to the development of foods with specific nutritional properties and includes:

- ❖ Development and rheological characterization of non-fermented gluten free dough.**
- ❖ Development of meat products including n-3 fatty acids**
- ❖ Development of reduced fat foods (coatings, emulsions).**

Development and rheological characterization of non-fermented gluten-free dough.

Research team:

Dra Alicia Califano

Dra Noemi Zaritzky

Ing. Gabriel Lorenzo

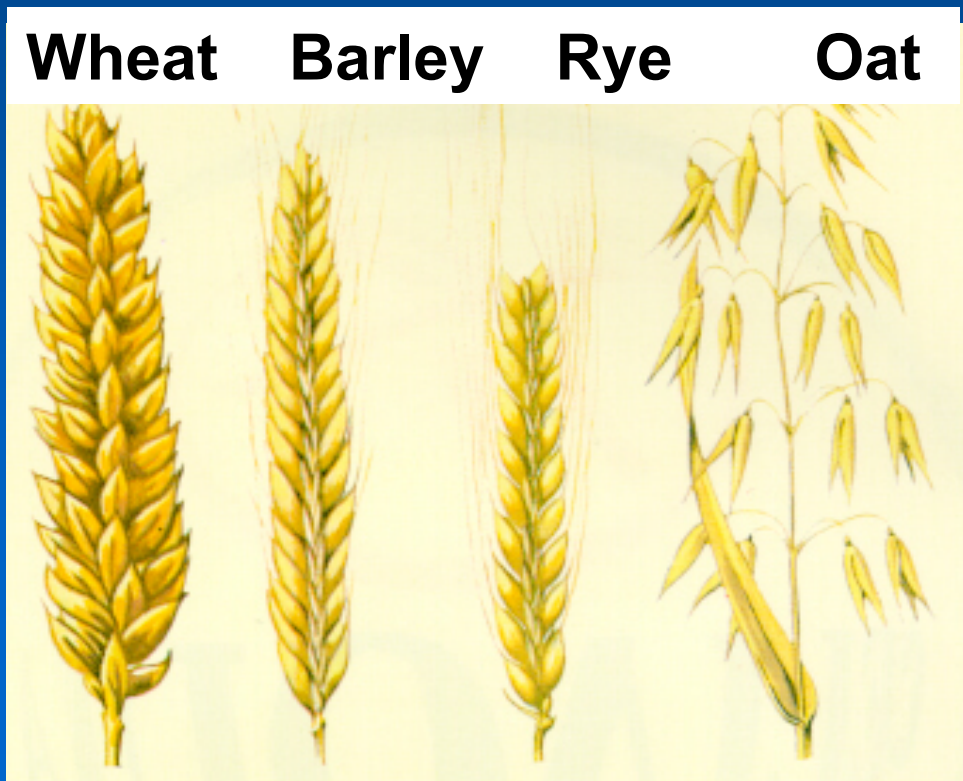


● **Celiac disease** is an autoimmune enteropathy caused by the ingestion of gluten-containing grains in susceptible individuals.

● Source : World Gastroenterology Organisation (WGO)

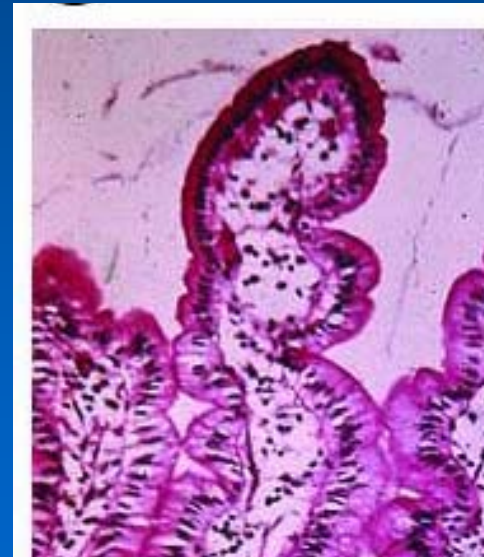
Celiac disease

- Gluten, found in **wheat**, includes two major protein types, the gliadins and glutenins, both of which contain celiac disease-activating peptides.



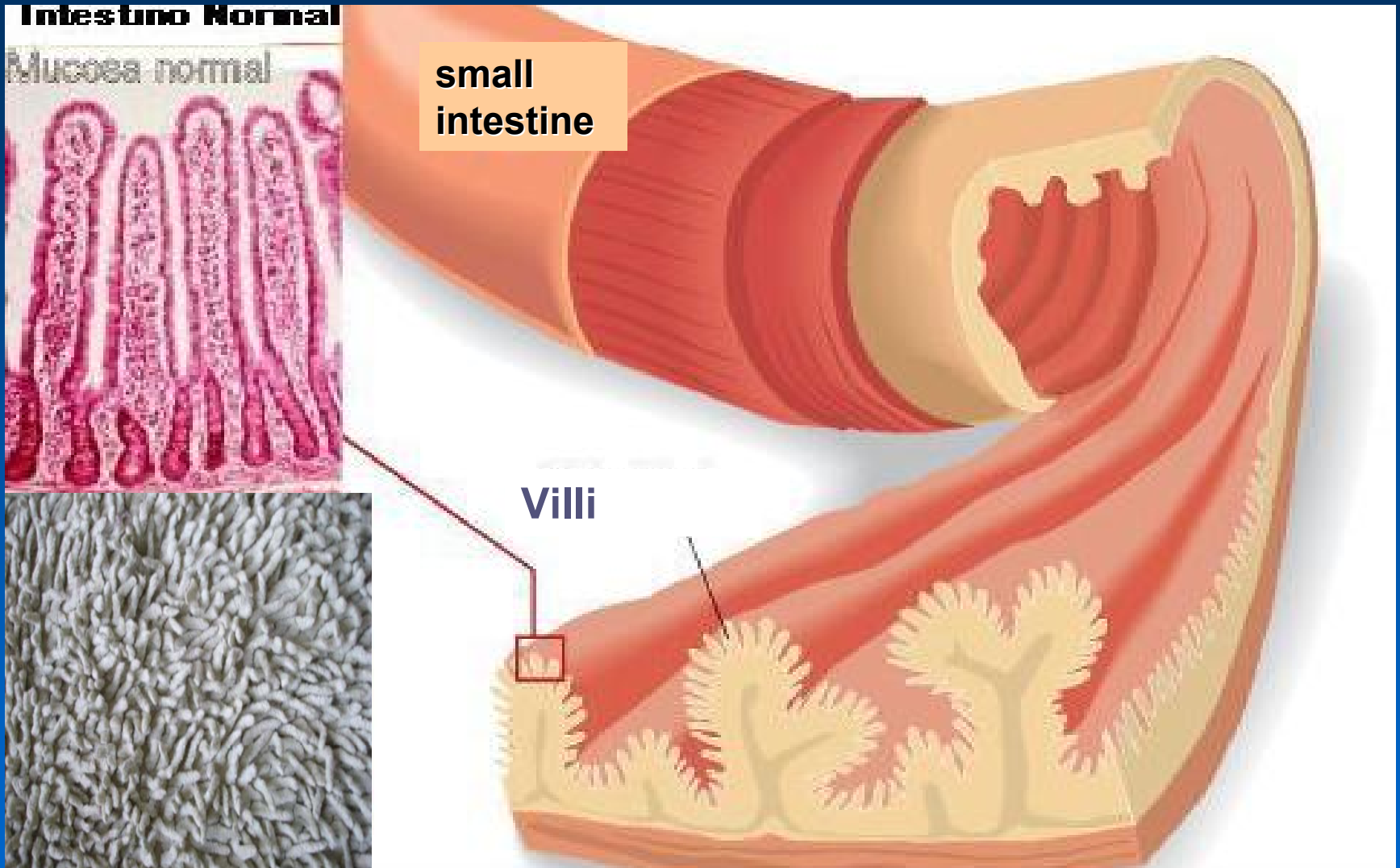
The closely related proteins in **barley** and **rye** that activate CD are the hordeins and secalins, respectively. Oats are thought to activate CD less frequently

The immune system cross-reacts with the small-bowel tissue, causing an inflammatory reaction that leads to a truncating of the villi of the small intestine (called villous atrophy).



**Normal small-intestinal
mucosal biopsy**

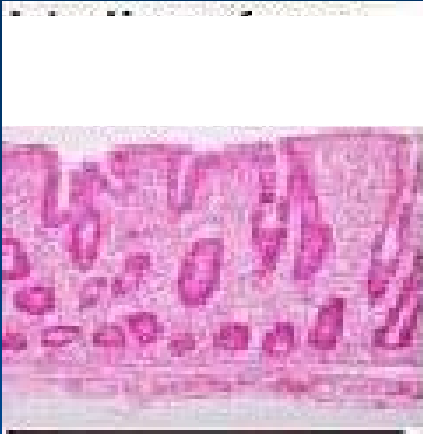
Small intestine **NORMAL VILLI**



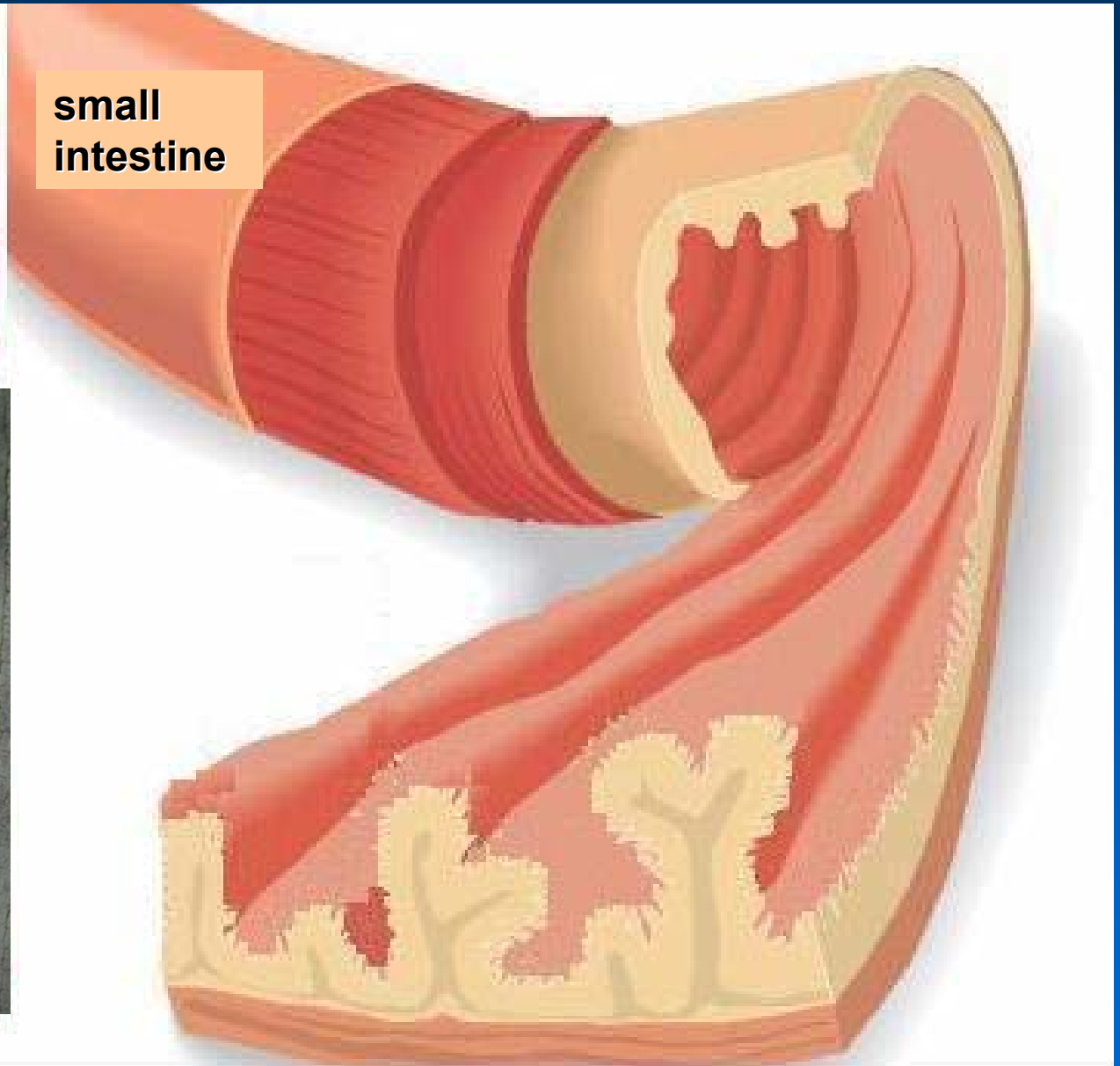
The villi are the fingerlike protrusions lining the small intestine and responsible for the absorption of nutrients

Celiac disease

TRUNCATION OF THE VILLI



small
intestine



Celiac disease is both a disease of malabsorption and an abnormal immune reaction to gluten.

What are the symptoms of celiac disease?

- Symptoms may occur in the digestive system or in other parts of the body.
- Digestive symptoms are more common in **infants and young children** and may include:
 - abdominal bloating and pain
 - chronic diarrhea
 - vomiting
 - weight loss
- Irritability is another common symptom in children.
- Malabsorption of nutrients during the years when nutrition is critical to a child's normal growth and development can result in other problems such as failure to thrive in infants, **delayed growth and short stature, delayed puberty, and dental enamel defects of the permanent teeth.**

- **Adults may have one or more of the following problems:**
- **Malnutrition and iron-deficiency anemia**
- **fatigue**
- **bone or joint pain**
- **arthritis**
- **bone loss or osteoporosis**
- **depression or anxiety**
- **infertility or recurrent miscarriage**
- **dermatitis herpetiformis.**
- **Long-term complications include, among other problems—liver diseases, and cancers of the intestine.**

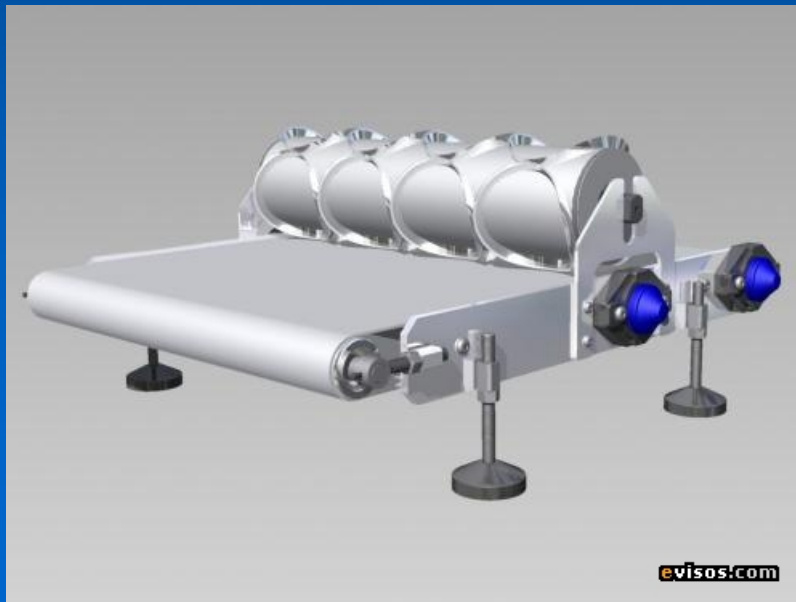
● **How common is celiac disease?**

- Celiac disease is a genetic disorder.
- About 1 in 133 people have the disease.
- Diagnosis rates are increasing.

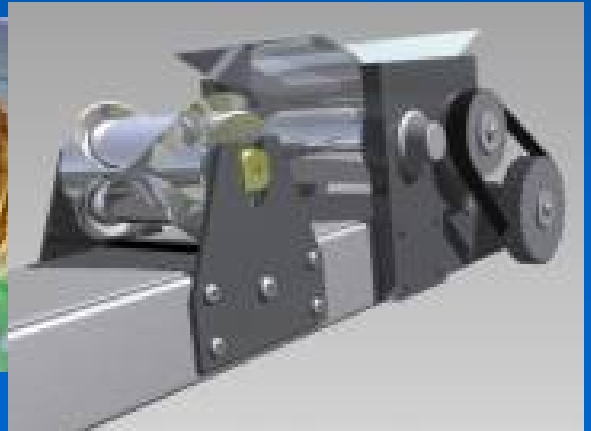
● **How is celiac disease treated?**

- The only treatment for celiac disease is a gluten-free diet.
- People with celiac disease must avoid gluten for the rest of their lives.

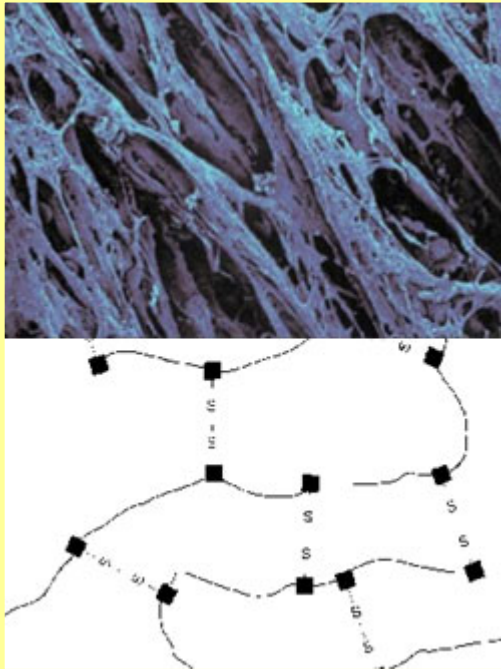
- **Non fermented dough** is used for pie crust and also to prepare a traditional meal in Latin America (“empanadas”). This dough normally includes wheat flour, fat, and water. Small disks (10 cm diameter) of pastry dough are filled with different componentes and folded. The pastry edges are firmly pressed together to seal the filling.
- The disks are industrially produced.



- The product is baked or fried before eaten.
- It is commercialized in two distinct ways, either as refrigerated disks of dough
- or “ready-to-bake” frozen “empanadas”.
- There is a very high commercial demand for such industrial products



- The problem is the low quality of the gluten-free dough currently in the market .
- It was necessary to conduct a research work in order to improve the rheological and mechanical properties associated to a poor structure.



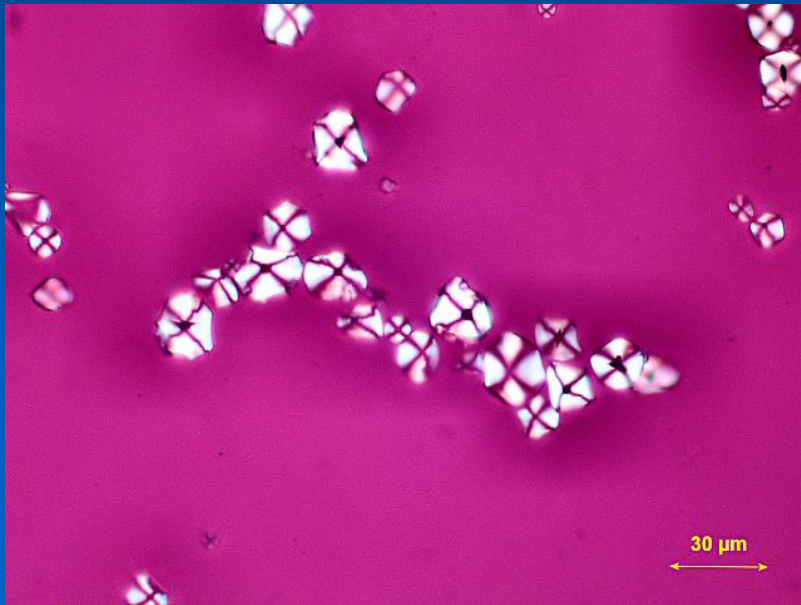
In order to develop free gluten products it must be considered that:

Gluten matrix is a major determinant of the properties of dough, thus it must be replaced with other network forming components, such as **hydrocolloids**.

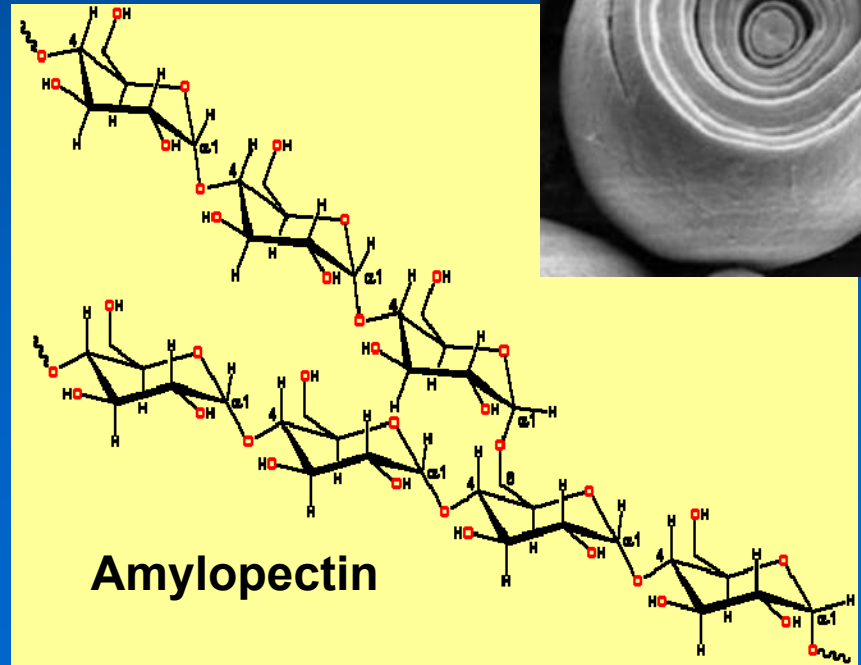
Development and rheological characterization of non-fermented gluten-free dough.

- Production of gluten-free non fermented pastries involves a research work to find an adequate combination of the key components **to produce a dough with a good elasticity, resistance to puncture, and stretching.**
- **Type of hydrocolloid and lipid phase** are two of the most important components, which affect the handling characteristics of the unbaked dough as well as the overall quality of the baked product.

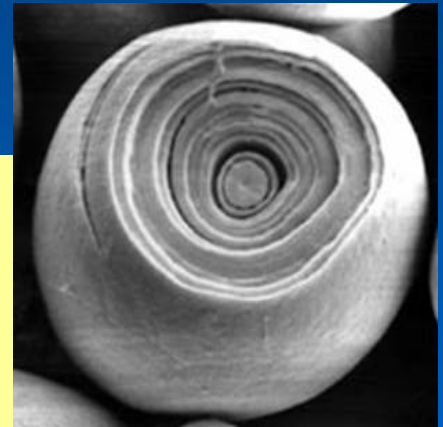
- **Theoretical and experimental progress in polymer and biomaterial science** has contributed to increase the knowledge of the processing – structure – rheology relationships of starch and others carbohydrates in food.



Corn starch



Amylopectin



- **The objectives of this reserach line were:**
- **To examine changes in the rheological attributes and viscoelastic behavior of non-fermented gluten-free dough as affected by composition and interactions between :**
- **Type of starch**
- **Type of hydrocolloid**
- **Lipid phase**

To consider the influence of :

- ✓ **the refrigerated storage time**
- ✓ **the freezing process**
- ✓ **baking stage**



Quality of the final product.

- **To perform complementary sensory evaluation of the product.**

Composition

% Proteins
(Whey protein concentrate)
% Water
% Hydrocolloids
% Lipid phase

Flour, starch

Corn starch
Cassava starch
Rice flour
Potato starch
Combinations

Analyzed variables

Hydrocolloids

Guar gum
Xanthan gum
HPMC (hydroxypropylmethylcellulose)
Combinations

Lipid Phase

• Sunflower oil,
• Low and high solid
content margarines

Texture analysis

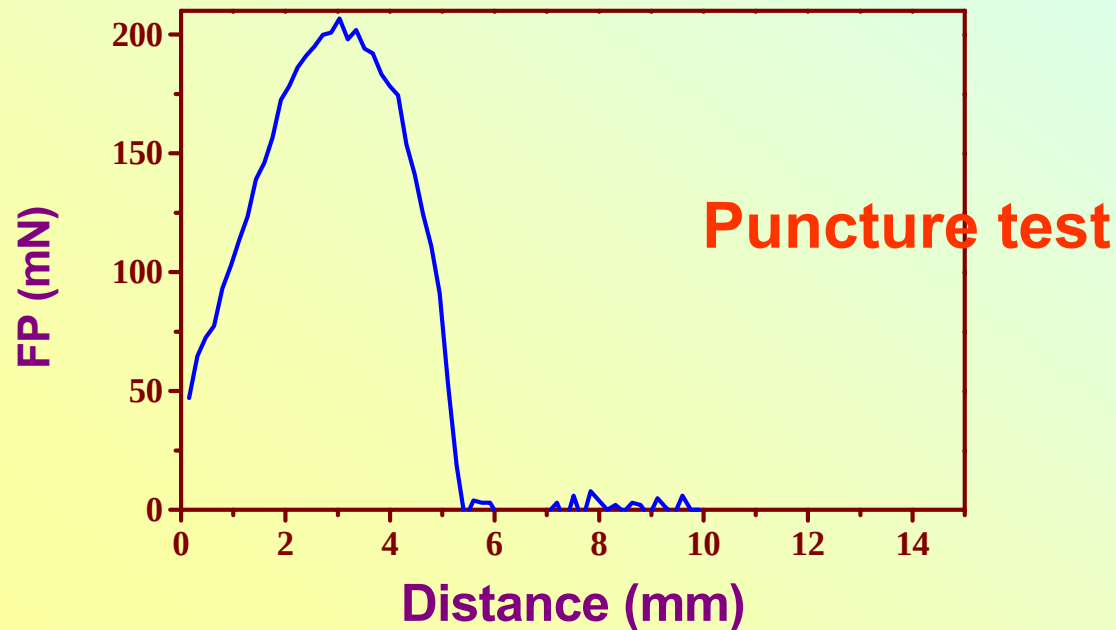
TAXT2i Texture Analyzer
(Stable Micro Systems,UK),
using the Texture Expert
Exceed software supplied
by Texture Technologies
Corporation .



➤ Puncture tests

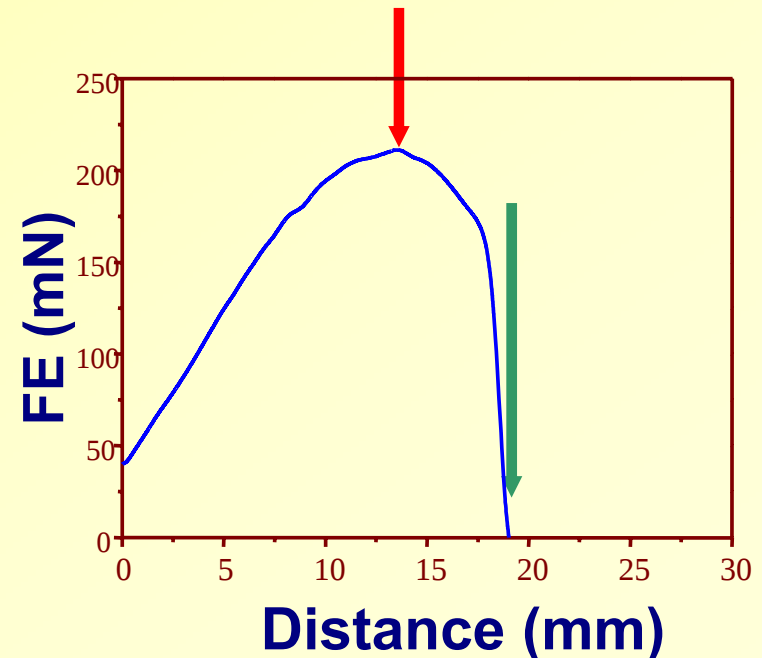
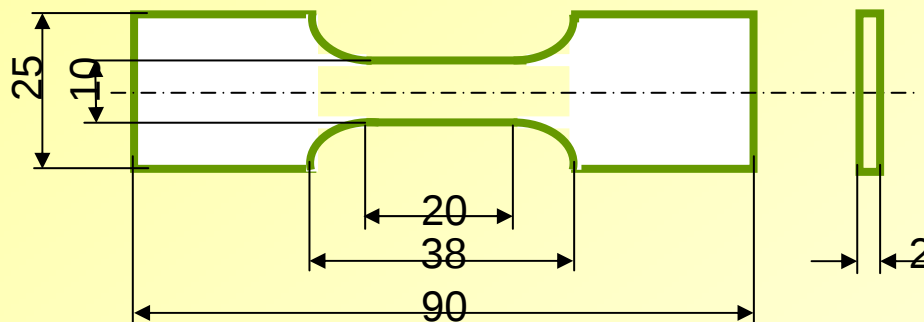
➤ Elongation tests

● Puncture tests. On raw specimens a cylindrical probe 2 mm in diameter at a constant rate of 1 mm/s was used. Tests were performed on disks of 40 mm diameter and 2 mm thick from each dough formulation (Lorenzo et al., 2008).



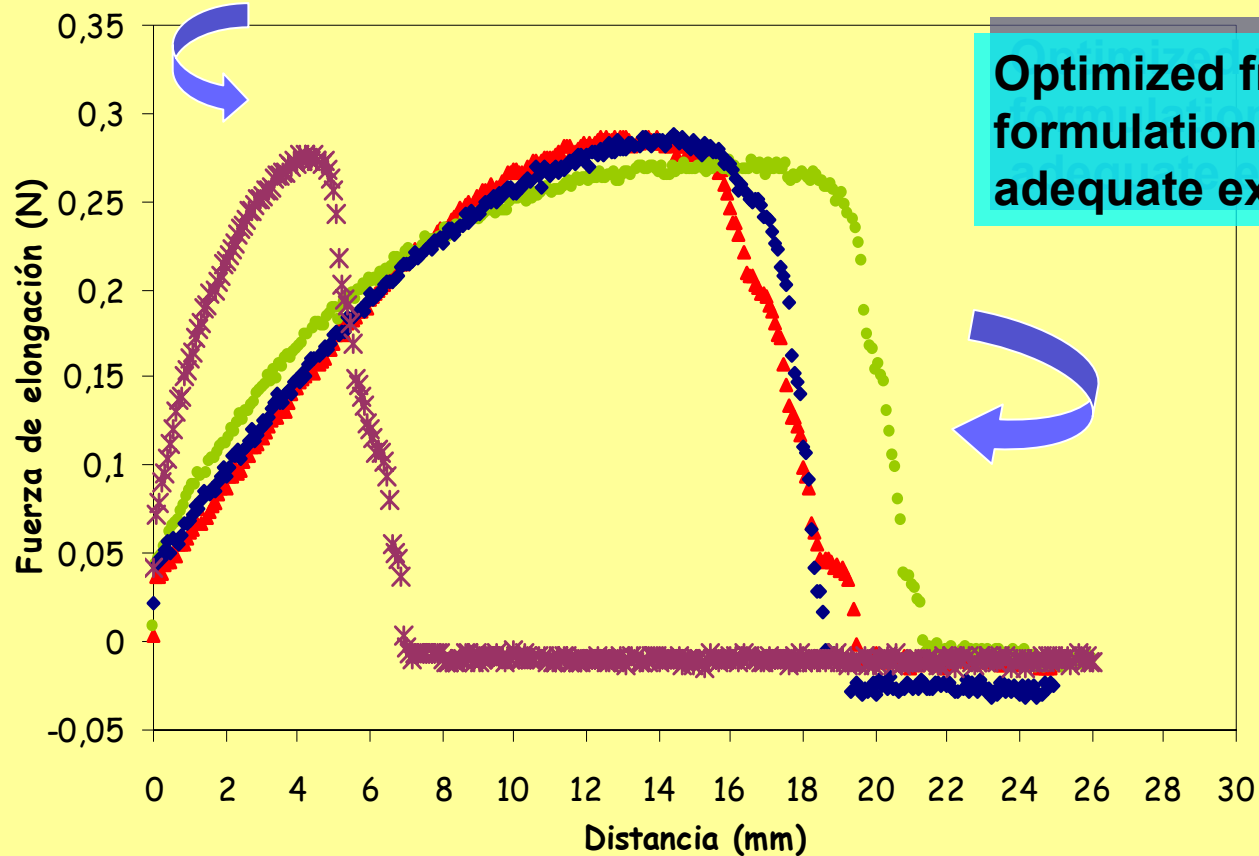
Elongation tests.

Tensile stress - strain relationships were determined by elongating a shaped specimen at a constant rate using a tension grip system A/TG while recording the load and elongation. Crosshead speed was set at 0.5 mm/s. **Maximum breaking force (FE) and deformation at break** (extension at the moment of rupture, D) was obtained from force vs. deformation curves.



Elongation test

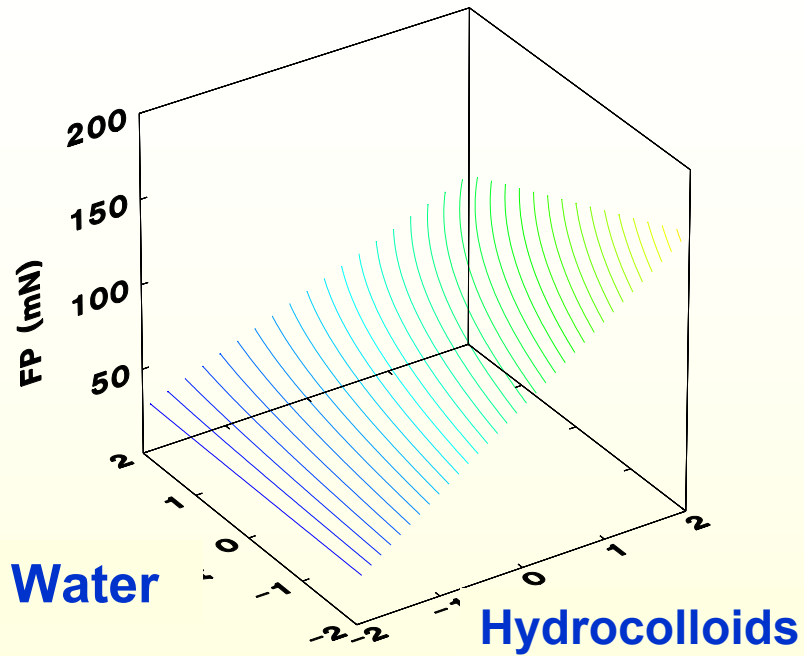
Commercial free gluten
formulation with low
extensibility



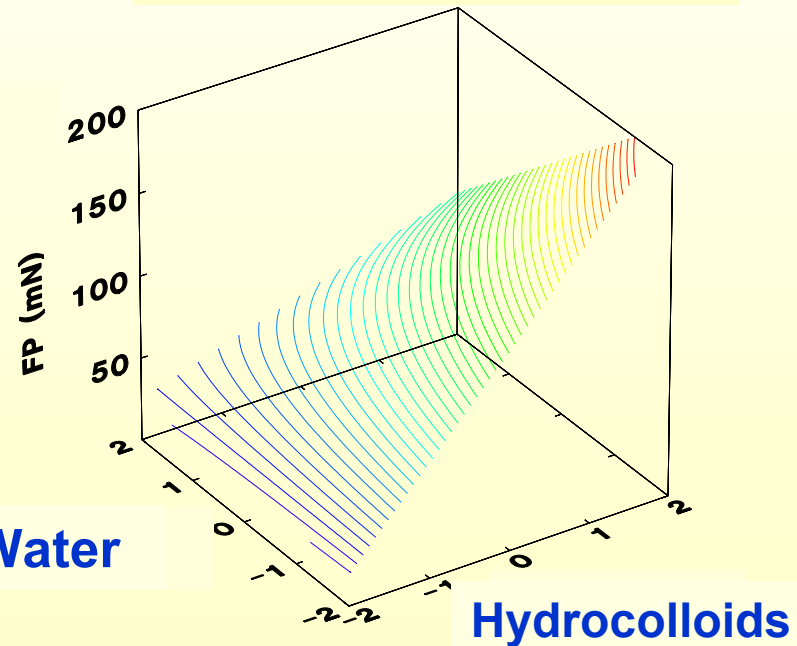
Optimized free gluten
formulations with an
adequate extensibility

Response surface

Puncture Test



**Protein
percentage >8%**



Viscoelastic behavior :

Small amplitude oscillatory shear tests

Controlled Stress
Rheometer RS600
(Haake, Germany)

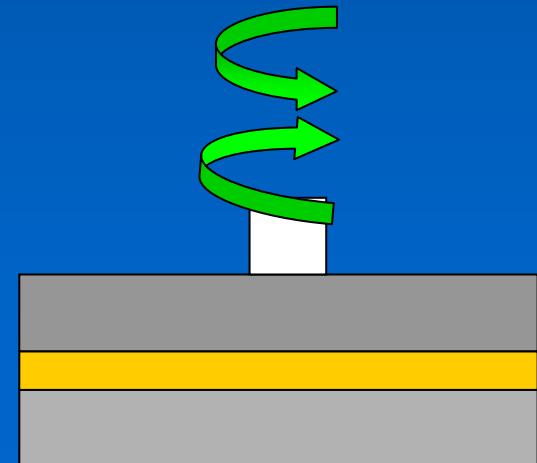


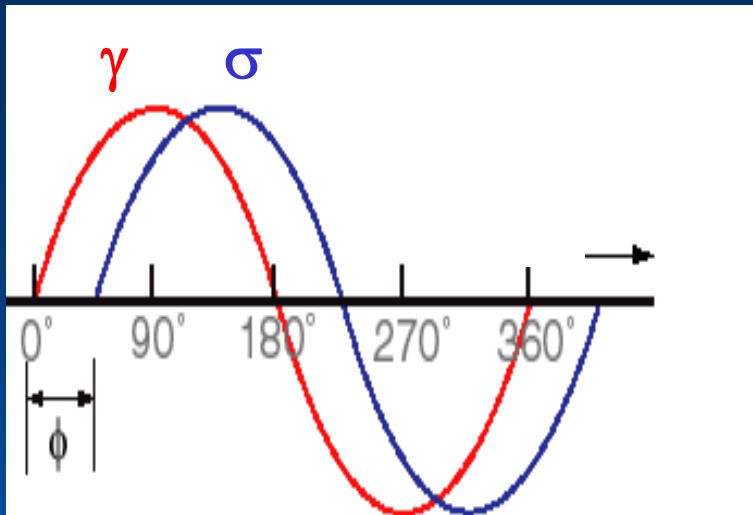
Oscillatory Deformation is applied

$$\gamma(\omega, t) = \gamma_0 \sin(\omega t)$$

Resulting stress is measured

$$\sigma(\omega, t) = \sigma_0 \sin(\omega t + \phi)$$





Phase angle ϕ

$\phi = 0^\circ$ ideal solids

$\phi = 90^\circ$ viscous ideal fluids
(newtonian)

$0 < \phi < 90^\circ$ viscoelastic systems

$G'(\omega)$ = Storage modulus (elastic component)

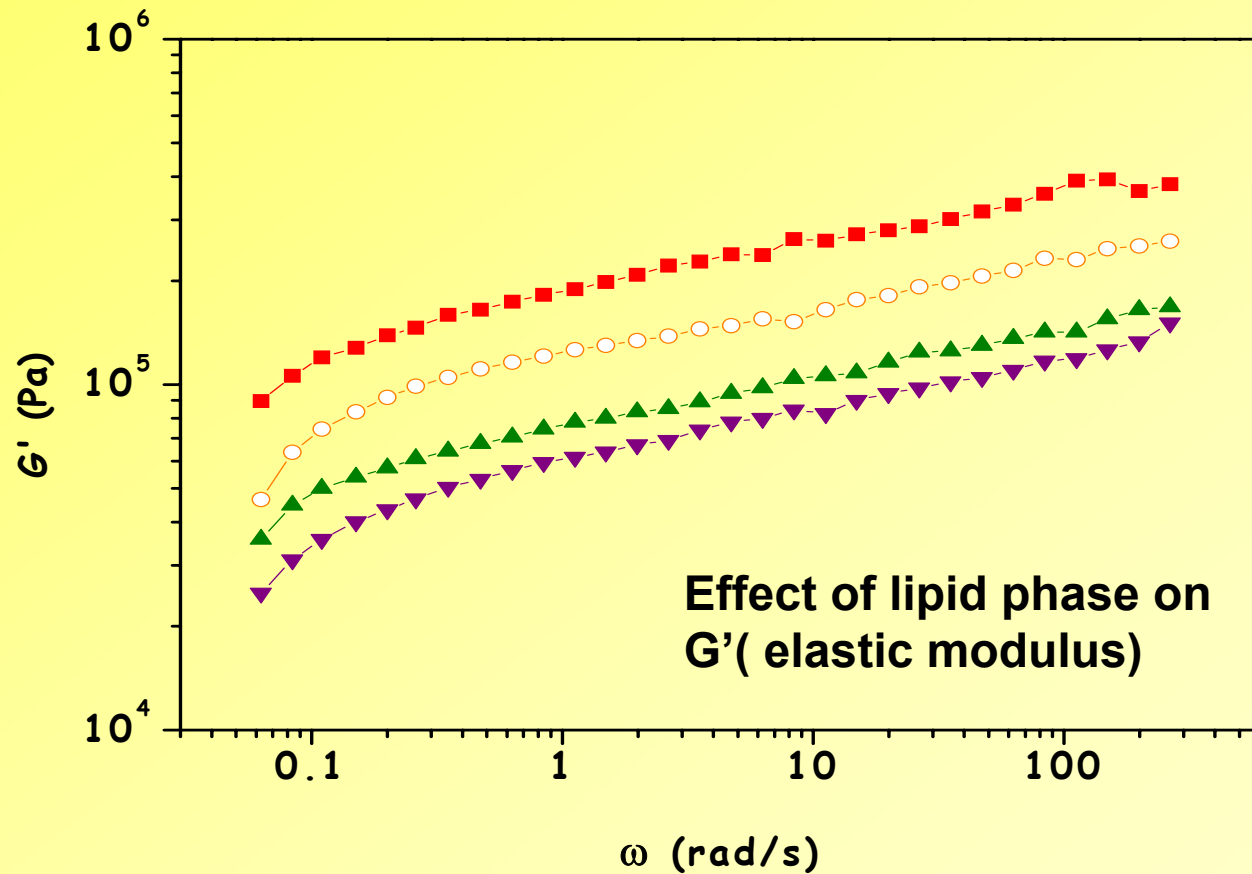
$G''(\omega)$ = Loss modulus (viscous component)

$$\tan \phi = G'' / G'$$

G^* = Complex modulus

$$G^* = (G'^2 + G''^2)^{1/2}$$

Dynamic oscillatory tests (Linear viscoelastic range)



Environmental scanning electron microscopy

Environmental Scanning electron microscope (Philip-Electroscan 2010, Netherland) was used to examine the dough samples

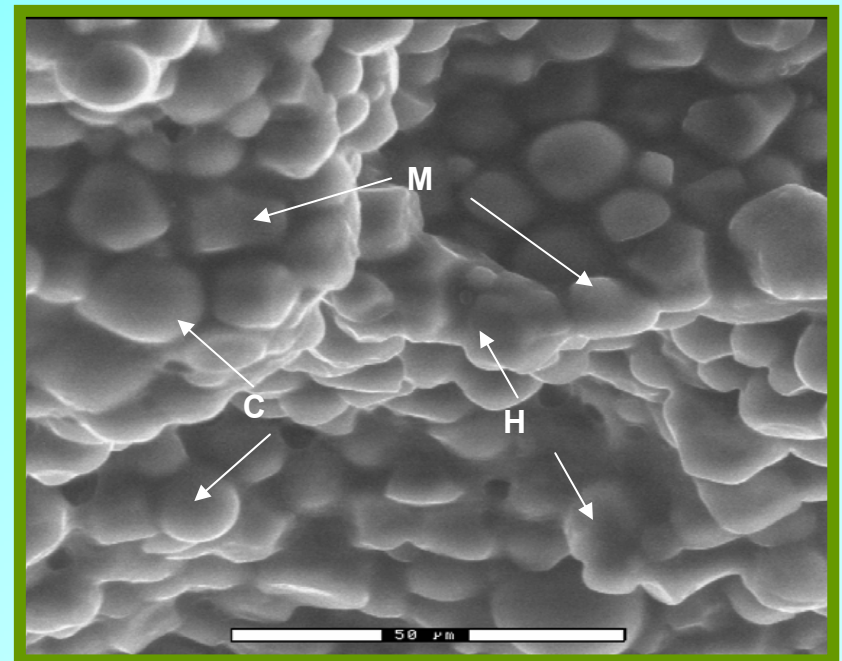
The micrograph shows a random organization of corn and cassava starch granules (raw sample) and a continuous hydrocolloids network

Bars = 50 μm

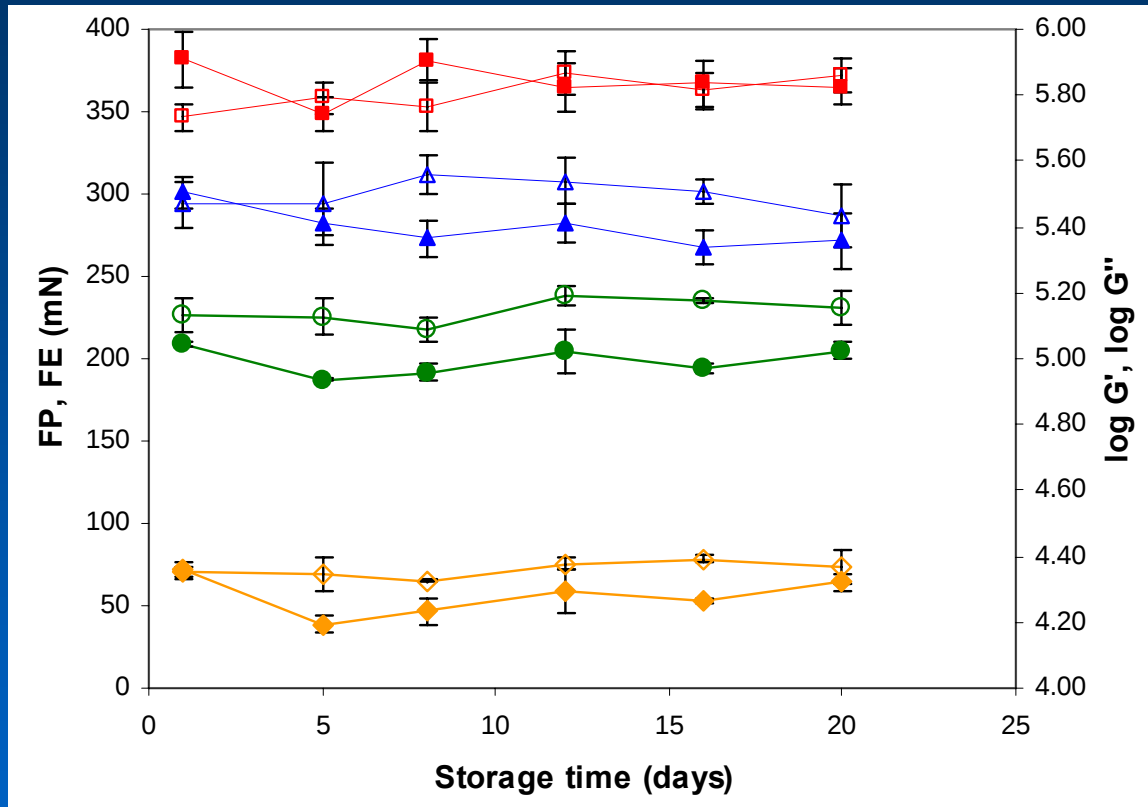
C = cassava starch;

M = corn starch;

H = hydrocolloid network



Effect of refrigerated storage on instrumental texture properties

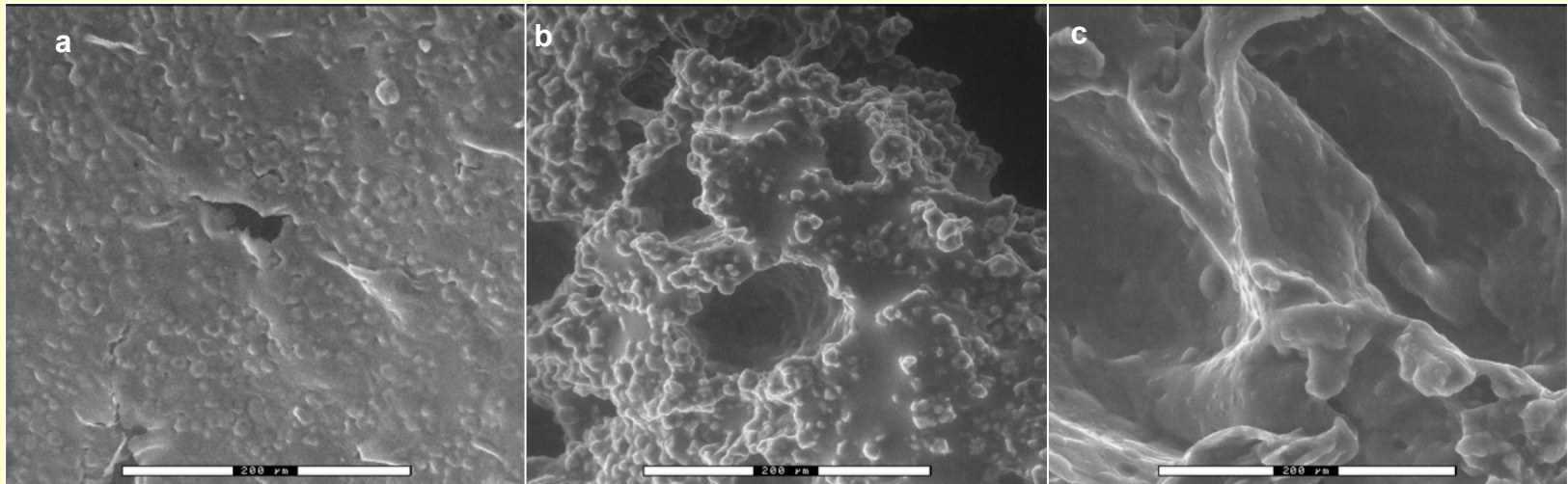


Optimized formulation

Puncture and elongation forces

Viscoelastic moduli

Environmental scanning electron microscopy (ESEM) of the baked dough



a: external surface, crust; b: middle region between the crust and the internal surface; c: internal surface.

Bar = 200 μm

➤ **Gluten-free doughs containing starches and hydrocolloids were satisfactorily formulated. Optimization of the formulation was based on rheological properties.**

➤ **These doughs, suitable for celiac people, showed a behavior appropriate for industrial production.**

➤ Freezing before baking did not alter the quality of the products. Hydrocolloids gave stability during freezing-thawing cycles, and help to minimize negative effects of the freezing and frozen storage of starch based products

➤ A sensory panel accepted the optimized formulation with a high score and it was significantly preferred over a commercial gluten-free dough.

PUBLICATIONS

- Lorenzo, G., Zaritzky, N., Califano, A. Optimization of non-fermented gluten-free dough composition based on rheological behavior for industrial production of “empanadas” and pie-crusts. **Journal of Cereal Science** 48, 224-231 (2008).
- Lorenzo, G., Zaritzky, N., Califano, A. Rheological characterization of refrigerated and frozen non-fermented gluten free dough: effect of hydrocolloids and lipid phase. **Journal of Cereal Science**, 2009 (in press)

LOW FAT FOODS

- A low-fat diet is one step toward a healthier lifestyle.
- Fat can raise cholesterol levels in the blood
- High-fat diets can lead to obesity and an increased risk of endometrial, bowel, breast and kidney cancer.
- Obesity increases the risk of heart disease and diabetes.

Innovations in the development of meat products formulated with n-3 fatty acids

Silvina C. Andrés,
Noemí E. Zaritzky and Alicia N. Califano

Cardiovascular Disease remains the main cause of death in both developed and developing countries, accounting for roughly 20% of all worldwide deaths per year.

It is recommendable the consumption of low fat products and to increase the intake of oils containing omega -3 fatty acids.

Meat products can be modified by adding ingredients considered beneficial for health or by eliminating or reducing components that are considered harmful such as saturated fat.

Fat content in processed meat products, such as sausages, can be readily reduced through formulation with leaner meats and/or by adding less fat to the formulation.

The major challenge in the development of reduced-fat food is to achieve fat reduction while matching as closely as possible the eating qualities of the traditional full fat products.

- ❖ Long chain polyunsaturated n-3 fatty acids (PUFA) have been implicated as critical nutrients for human health.
- ❖ Oils rich in n-3 PUFA are present mainly in cold water fish and seafood.
- ❖ Fish oils contain the longer-chain omega-3 fatty acids eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA).
- ❖ Although the body to some extent can convert ALA alpha-linolenic acid into these longer-chain omega-3 fatty acids, the omega-3 fatty acids found in marine oils help fulfill the requirement of essential fatty acids
- ❖ Fortification of foods with these fatty acids is an important emerging area of commercial and academic interest

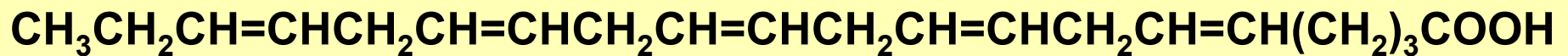
Omega -3 poliunsaturated fatty acids

α -Linolenic acid (ALA)



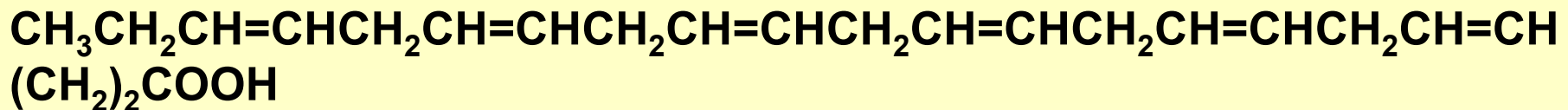
cis,cis,cis- $\Delta^9, \Delta^{12}, \Delta^{15}$ 18:3 $n-3$

Eicosapentaenoic acid (EPA)



cis,cis,cis,cis,cis- $\Delta^5, \Delta^8, \Delta^{11}, \Delta^{14}, \Delta^{17}$ 20:5 $n-3$

Docosahexaenoic acid (DHA)



cis,cis,cis,cis,cis,cis- $\Delta^4, \Delta^7, \Delta^{10}, \Delta^{13}, \Delta^{16}, \Delta^{19}$ 22:6 $n-3$

- **Incorporation of n-3 PUFA into food systems is potentially problematic due to their propensity to readily oxidize.**
- **Poultry products have a high potential to reduce their fat content and to include polyunsaturated fatty acids.**
- **The development of low-fat products rich in polyunsaturated fatty acids to replace traditional ones may contribute to a more healthful diet.**

- **The objectives of this research line were:**
 - **To develop low-fat poultry sausages enriched in polyunsaturated fatty acids by replacing fat with squid oil.**
 - **To characterize their physico-chemical, textural, and sensory properties**
 - **To compare the quality attributes of low fat poultry sausages containing beef tallow as lipid source, with those containing squid oil.**
 - **To evaluate in the case of squid oil formulated products, the fatty acid profile and rancidity.**

- ❖ Low-fat sausages were developed using fresh poultry breast meat (pH: 5.7-5.9).
- ❖ **Lipid concentration: 5 g/100 g**
- ❖ The combined total fat and added water content cannot exceed 40%, whereas the traditional level was 30%fat and 10% added water (USDA-FSIS, 1990).
- ❖ **Deodorized refined squid oil (SO)** with 1 g/kg of synthetic vitamin E. Fatty acid (FA) composition of the SO was: monounsaturated (MUFA) 31.81 %; saturated (SFA) 24.97 %; **polyunsaturated (PUFA) 40.88 % and n-3 PUFA 37.87 %** (eicosapentaenoic acid, EPA, 9.96 % and docosahexaenoic acid, DHA, 24.86 %),
- ❖ **Commercial beef tallow.** Fatty acid composition : **saturated fatty acid SFA 56.10 %; MUFA 35.8 % and PUFA 5.7 %**
- ❖ **Added Hydrocolloids: xanthan and guar gums (0.3g/100g)**
- ❖ **Whey protein concentrate (1g/100g)**

Fatty acids of squid oil

Fatty acid	%
C14:0	3.16
C14:1	0.27
C15:0	0.40
C15:1	0.14
C16:0	13.69
C16:1	8.84
C16:2	0
C16:3	1.42
C16:4	0.83
C17:0	1.66
C17:1	0.70
C18:0	1.90
C18:1	17.66
C18:2 n6	2.19
C18:3 n3 (ALA)	0.64
C18:4 n3	1.59

C20:0	0.05
C20:1	1.94
C20:2 n6	0.40
C20:3 n6	0.26
C20:3 n3	1.27
C20:4 n6	0.06
C20:4 n3	0.55
C20:5 n3 (EPA)	9.96 
C22:1 n11	0.87
C22:1 n9	0.60
C22:1	0.23
C22:2	0.44
C22:5 n6	0.47
C22:5 n3	1.90
C22:6 n3 (DHA)	24.86 

**Manufacture: Manually stuffed in collagen
reconstituted casing**

Hand-linked



**Heat-processed in
“cook-in” bags in 80°C
water bath (74°C final
internal temperature)**



**Cooling in ice-
water bath**



**Vacuum packaged in EVA/SARAN/EVA
film and stored at 4°C**



METHODS OF ANALYSIS

- ❖ Proximate composition

- ❖ Process yield

Storage stability of the refrigerated vacuum packaged product (4 °C) by measuring :

- ❖ Color (Minolta colorimeter L*, a*, and b*)

- ❖ Texture (Texture Profile Analysis TPA TAXT2i Texture Analyzer, Stable Micro Systems, UK)

- ❖ Microstructure (SEM)

- ❖ Purge loss during refrigerated storage

- ❖ Microbial counts

- ❖ Sensory Analysis (25 panellists, flavor, texture and overall acceptability characteristics)

- ❖ Fatty acid profile (Gas Chromatography)

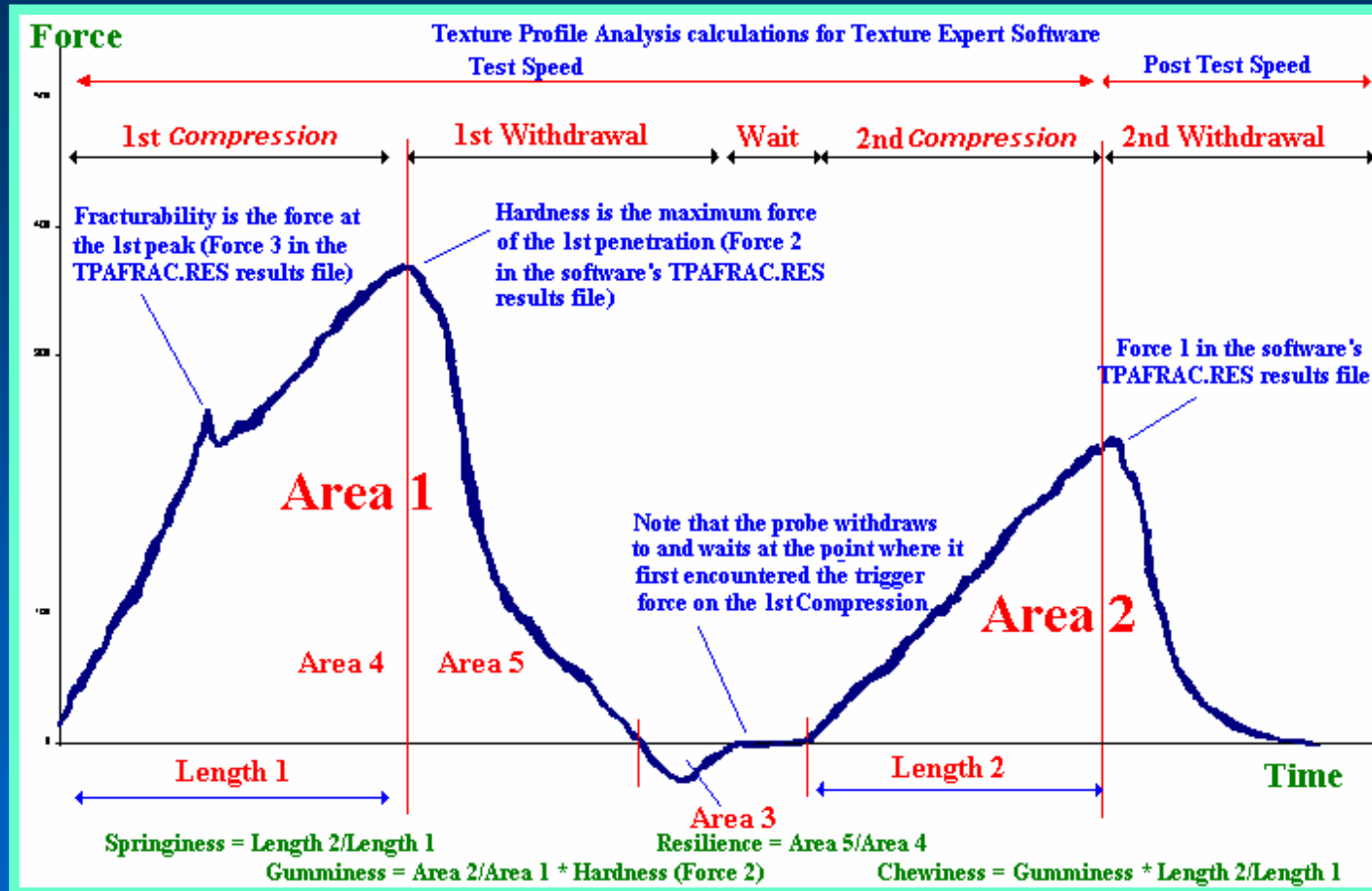
- ❖ Lipid oxidation (Thiobarbituric acid reactive substances (TBARS) (mg malonaldehyde (MDA)/kg product).

- ❖ Low-fat poultry sausages containing 5 % of refined squid oil with antioxidants was compared to those containing 5 % of beef tallow.
- ❖ Water content = 74 - 79 %; Proteins=12-14%
- ❖ Both products showed very good stability and quality attributes.
- ❖ The incorporation of hydrocolloids and whey protein concentrate contributed to obtain high process yields (97%) and low purge losses during refrigerated storage .

Sausages with squid oil presented :

- ❖ higher lightness, lower redness and yellowness than the formulation prepared with solid fat.

TPA (Texture Profile Analysis)



Cohesiveness: $\text{area2} / \text{area1}$

Elasticity: $\text{dist. 2} / \text{dist.1}$

Resilience: $\text{area 5} / \text{area4}$

Masticability: $\text{area 2} \times \text{dist2} / (\text{area1} \times \text{dist.1})$

Hardness (peak force of first compression cycle, N)

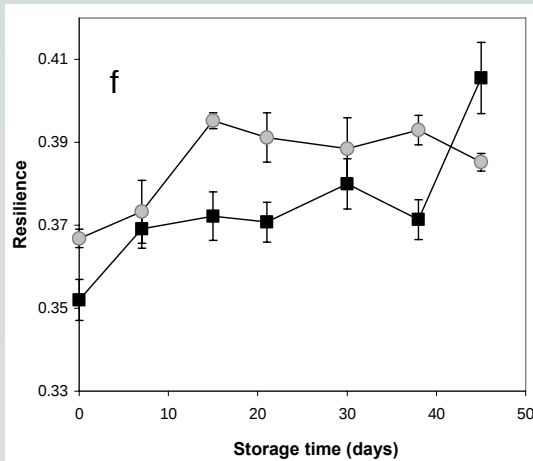
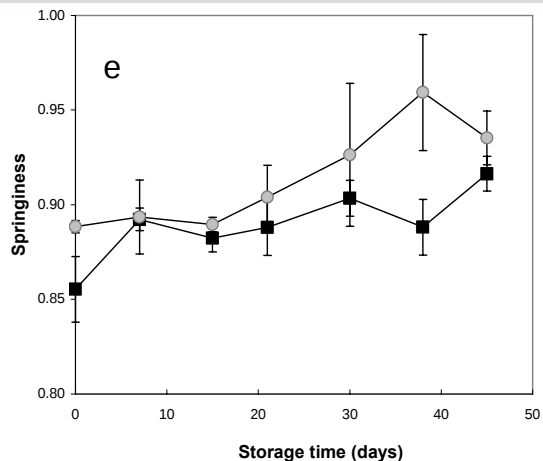
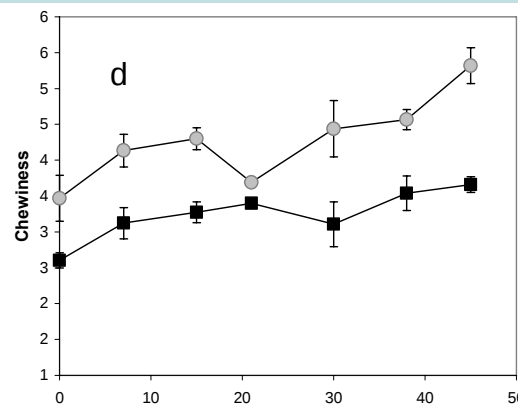
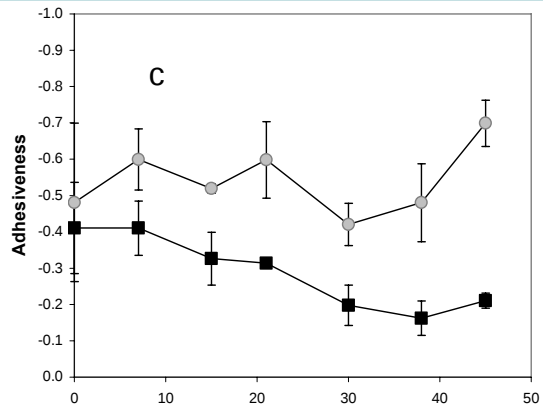
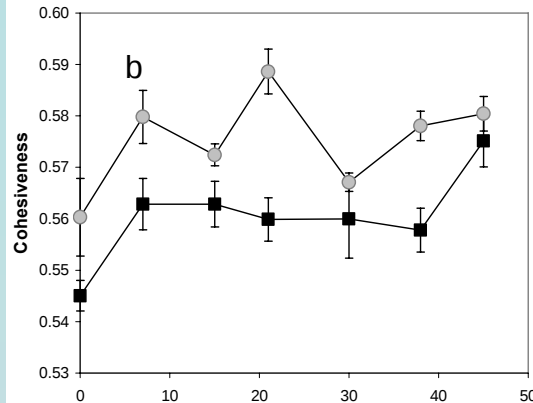
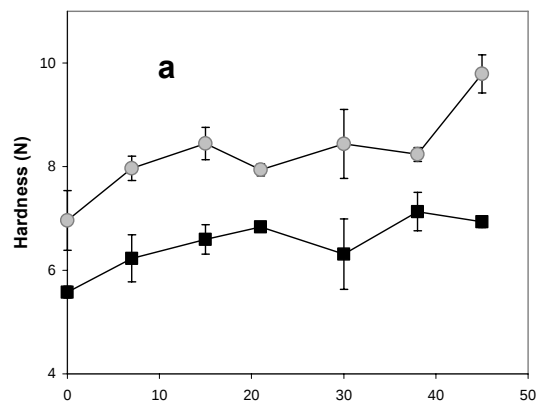
Springiness (distance of the detected height of the product on the second compression divided by the original compression distance, mm/mm),

Cohesiveness (ratio of positive areas of second cycle to area of first cycle, J/J),

Adhesiveness (negative force area of the first byte represented the work necessary to pull the compressing plunger away from the sample, J),

Chewiness (hardness x cohesiveness x springiness, N),

Resilience (area during the withdrawal of the first compression divided by the area of the first compression, J/J)



Effect of refrigerated vacuum storage time on Texture Profile Analysis parameters of SO (■) or BT (●) poultry sausages:

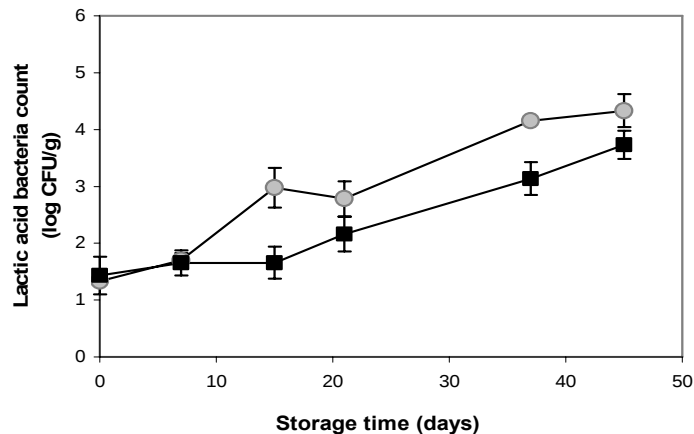
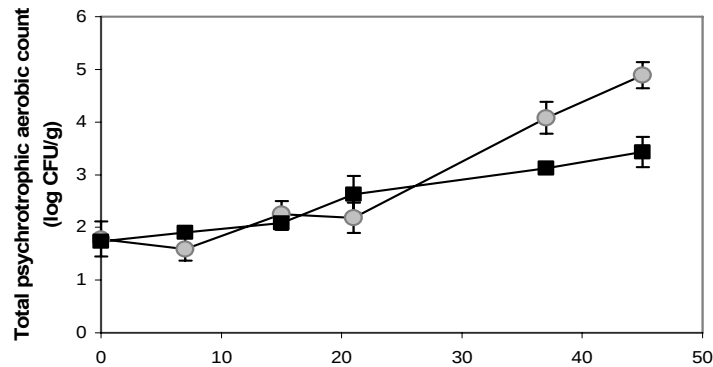
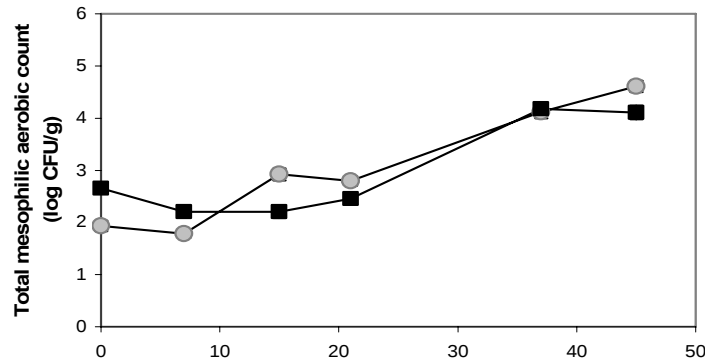
a) hardness, b) cohesiveness, c) adhesiveness, d) chewiness, e) springiness, f) resilience. Error bars indicate SEM.

The product formulated with squid oil showed lower values of :

- **Hardness**
- **Cohesiveness**
- **Adhesiveness,**
- **Chewiness**
- **Resilience.**

Microbial counts

- **Total mesophilic aerobic counts:** PCA incubated at 30 °C for 2 days.
- **Total psychrotrophic aerobic counts:** PCA incubated at 4 °C for 7 days
- ***Enterobacteriaceae*:** Violet Red Bile Agar (Merck) incubated at 37°C for 24 h.
- **Lactic acid bacteria:** Man Rogosa Sharp Agar (MRS, Oxoid) incubated at 30 °C for 2 days.
- **Mould and yeast counts:** Yeast Glucose Cloranfenicol Agar (YGC) (Merck) incubated for 5 days at 30 °C.
- Data were expressed as log colony forming units (CFU)/g sample.
- **Total coliform counts** using the most probable number (MPN) method according to AOAC (1984) method 46016,
- **Sulfite-reducing Clostridium counts** were enumerated in TNS agar (Biokar Diagnostics) incubated at 37°C for 48h in anaerobic condition.



Effect of refrigerated storage time on microbial growth of vacuum packaged SO (■) or BT (●) poultry sausages:

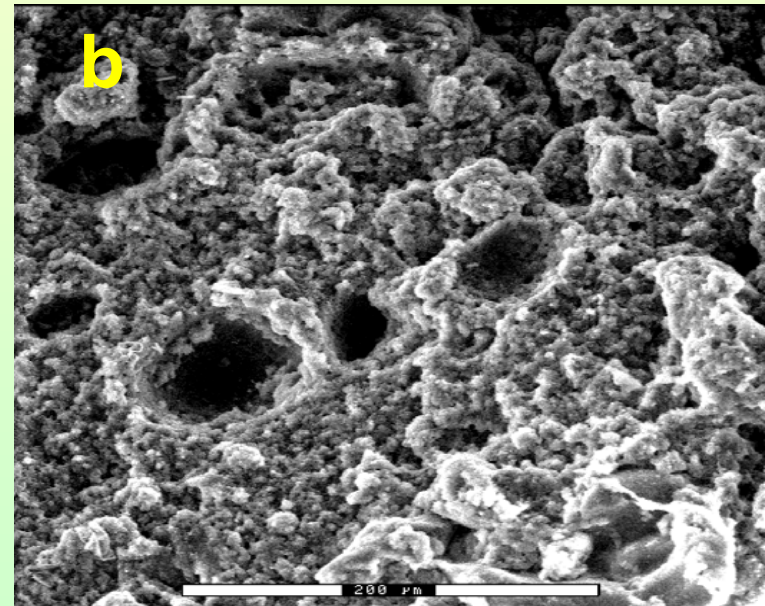
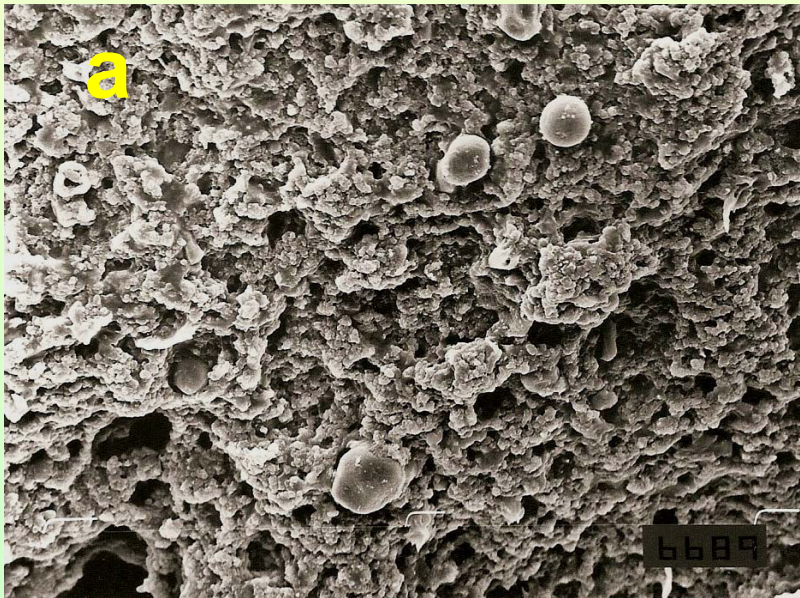
a) total mesophilic aerobic counts, b) total psychrotrophic aerobic count, c) lactic acid bacteria counts. Error bars indicate SEM.

Microbial counts of both products were lower than 5 log CFU/g at the end of 90 days of storage at 4°C.

**No coliforms were detected
No sulfite-reducing
Clostridium were detected.**

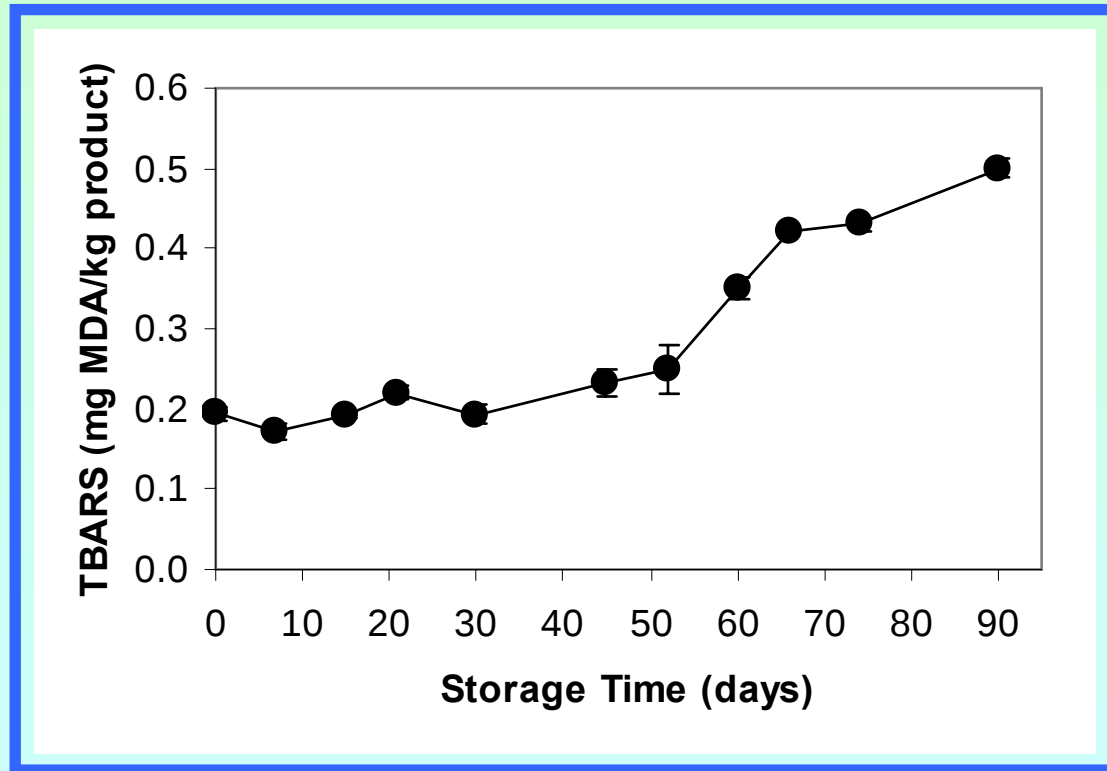
MICROSTRUCTURE (SEM)

Micrographs of BT and SO sausages. Cohesive and somewhat granular protein matrixes were observed. Fine strands and sheets with gel-like appearance were observed, probably caused by the addition of whey protein and hydrocolloids to the formulation. Fat globules were visible in BT sausages, however, there were not visible in SO ones.



Scanning electron micrographs of BT (a) or SO (b) poultry sausages.
a) Bar = 100 μm ; b) Bar = 200 μm . F= fat globule

Low lipid oxidation was observed mainly due to the combined effect of the antioxidant (synthetic vitamin E) included in the squid oil to stabilize the n-3 PUFA, vacuum packaging, and low storage temperature



Changes in TBARS values of poultry sausages with 5 % squid oil during storage expressed as mg MDA/kg product. Error bars indicate SEM.

- ❖ Sausages formulated with squid oil will be healthier due to the high PUFA, and low SFA contents, in addition to low total fat content.
- ❖ The predominant n-3 PUFA was Docosahexaenoic acid, DHA (16-18 g /100g), followed by Eicosapentaenoic acid EPA (7-9 g/100 g) and Linoleic acid (C18:2, n-6, 5-7 g/100g).
- ❖ Energy value ranged between 123 and 128 kcal/100 g, less than half the 315 kcal/100 g of the traditional products
- ❖ The good sensory results obtained for flavor, texture and overall acceptability of squid oil formulated sausages showed that the presence of this unsaturated fatty acids rich oil did not adversely affect the product, leading to an innovative and healthier product.

PUBLICATIONS

- ❖ The effect of whey protein concentrates and hydrocolloids on the texture and colour characteristics of chicken sausages. SC Andrés, NE Zaritzky, AN Califano. *International Journal of Food Science and Technology* 41, 954-961(2006).
- ❖ Storage stability of low-fat chicken sausages.S.C. Andres , M.E. García, N.E. Zaritzky. A.N. Califano. *Journal of Food Engineering* 72 (2) 311-319. (2006).
- ❖ Stress relaxation characteristics of low-fat chicken sausages made in Argentina.Silvina C. Andres, Noemi E. Zaritzky, Alicia N. Califano. *Meat Science*, 79 (2008) 589–594
- ❖ Innovations in the development of healthier chicken sausages formulated with different lipid sources.S. C. Andrés, N. E. Zaritzky,A. N. Califano. *Poultry Science*. (in press 2009)

Edible coatings acting as oil barriers

- ✓ The **reduction of the lipid content in fried foods** is required mainly owing to its relation with obesity and coronary diseases.
- ✓ An alternative to reduce oil uptake in fried foods is the use of **edible coatings**.

Research team:

Garcia A.
Bertola N.
Ferrero C.
Campañone L.
Martino
Zaritzky N.



- **Edible coatings are useful materials produced mainly from edible biopolymers and food-grade additives (GRAS)**
- **Coatings are a particular form of films directly applied to the surface of materials.**
- **An edible coating has a close and continuous association with the food until consumption.**
- **Coatings are regarded as a part of the final product and can be used as a host for additives in the conservation of the food properties or in order to improve the food quality**

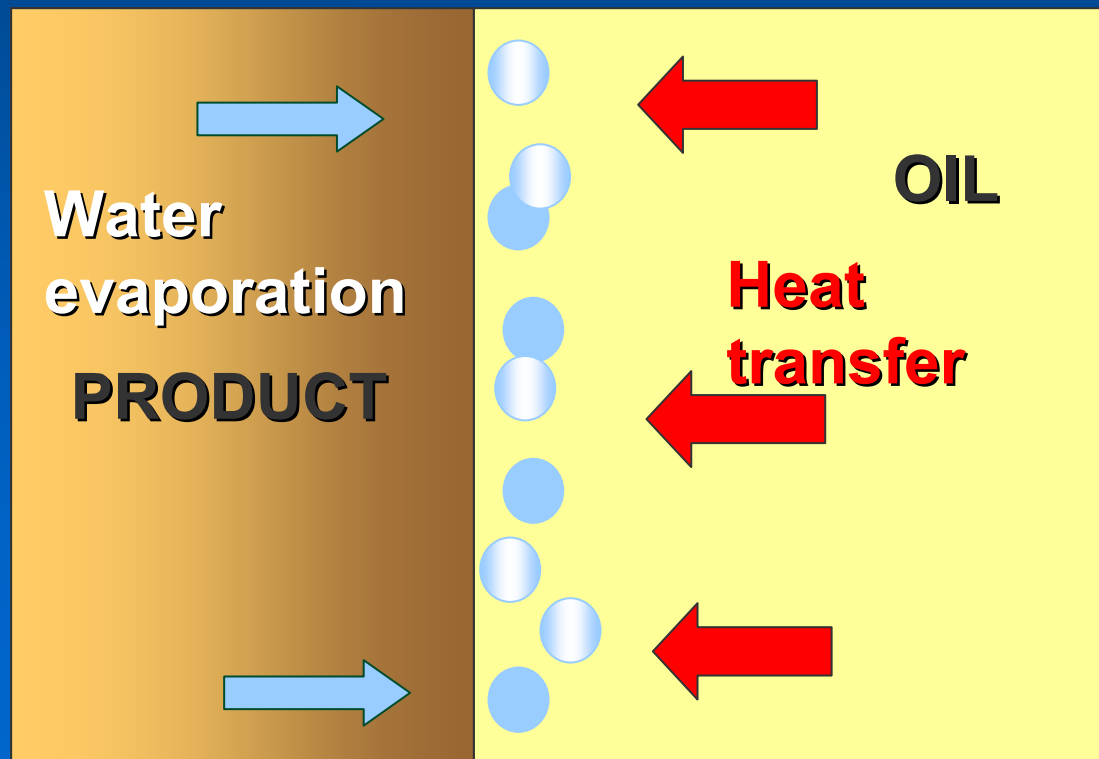
✓ **Frying occurs during the immersion of the product in oil at a temperature higher than the boiling temperature of water (150- 200°C)**

The study of the frying process, is important because of:

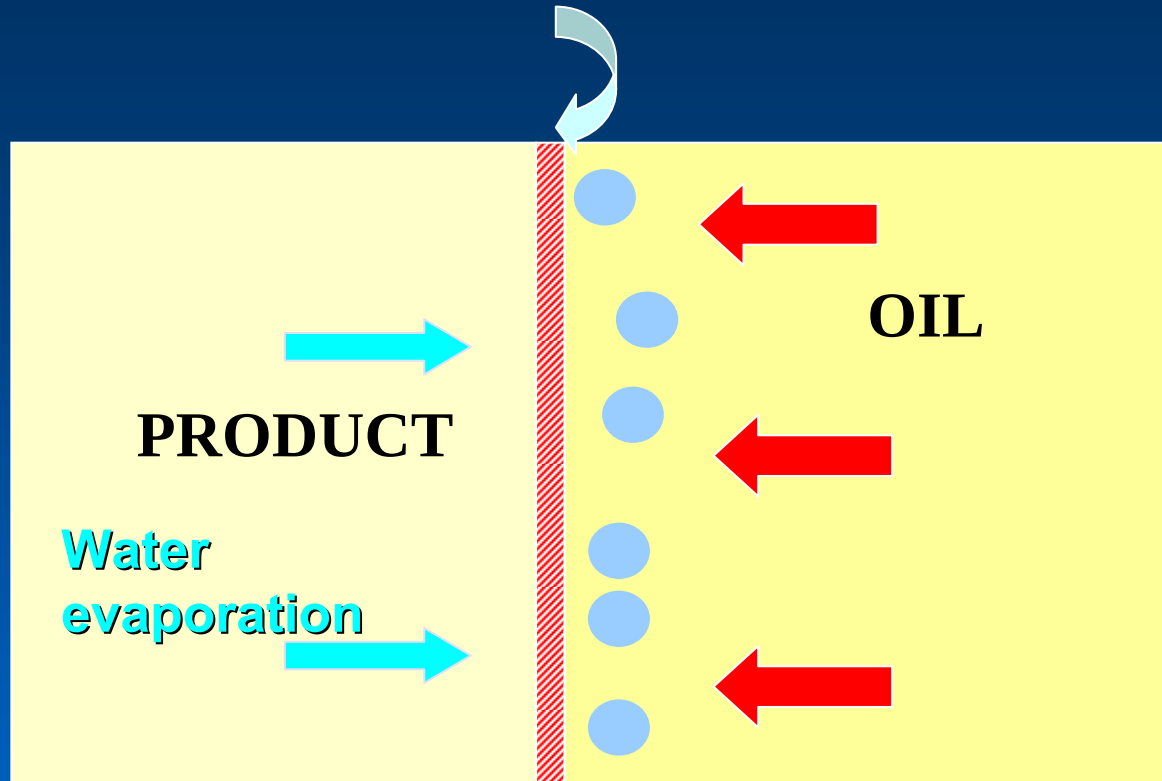
✓ **the great volume of production of fried foods (economical impact)**

✓ **the influence on the consumption of lipids (related to nutritional aspects)**

- ✓ Deep-fat frying is a complex process involving simultaneous heat and mass transfer.
- ✓ The process induces a variety of physicochemical changes in both, the food and the frying medium.

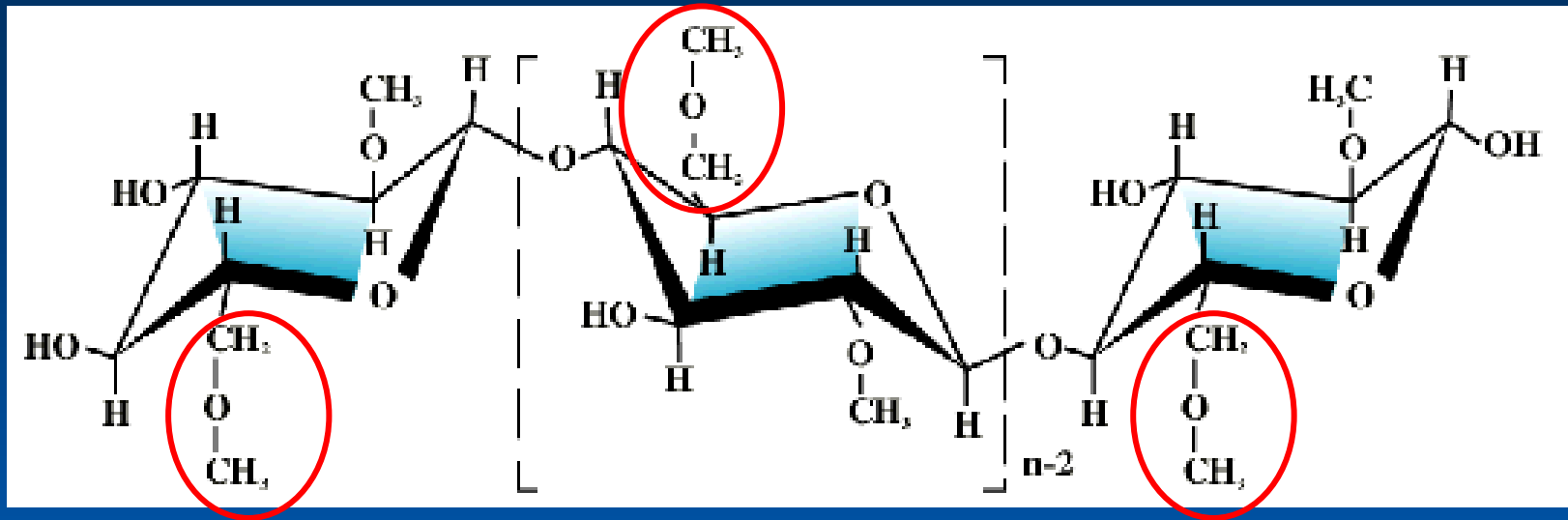


What is the effect of an edible coating?



- ✓ The application of **coatings** allows the oil content reduction in deep-fat fried products.

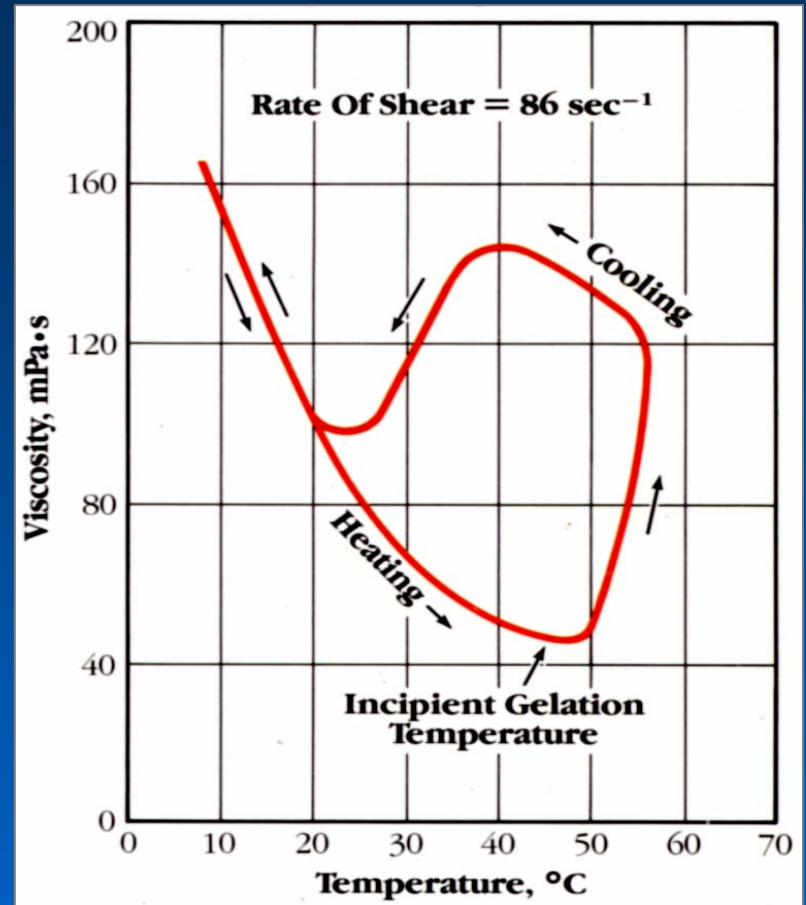
Methylcellulose



Methylcellulose is a methyl ether of cellulose, arising from substituting the hydrogen atoms of some of cellulose's hydroxyl groups $-OH$ with methyl $-CH_3$, forming $-OCH_3$ groups.

Cellulose derivatives, including **methylcellulose** (MC) and **hydroxypropyl-methylcellulose** (HPMC) exhibit **thermal gelation**.

When suspensions are heated, they form a gel that reverts below the gelation temperature, and the original suspension viscosity is recovered.



MC forms a gel at high temperatures. Hydrophobic polymer chain interactions were involved in the thermal gelation process with a dominance of inter-molecular H bonding over intra-molecular H bonding within the cellulose ether

Dough Discs : were prepared with refined wheat flour and distilled water.

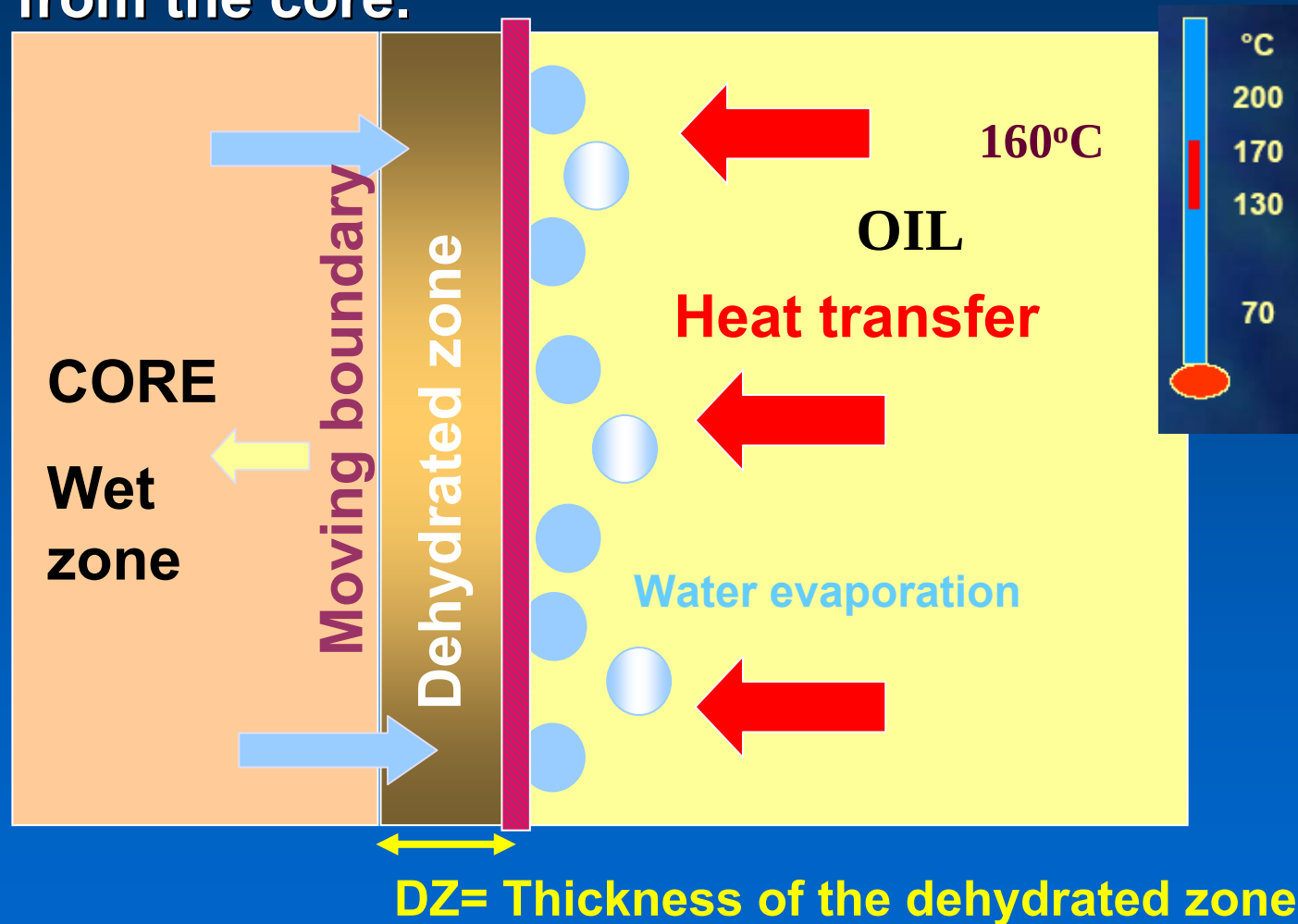
Edible Coating Formulation: 1% (w/w) MC aqueous solution and 0.75 % (w/w) sorbitol

Dough samples were dipped in the coating suspensions for 30 seconds.

Uncoated (control) and coated samples were fried in a controlled temperature deep-fat fryer ($160 \pm 0.5^\circ\text{C}$)



❖ During frying a moving boundary is produced within the product separating the dehydrated zone from the core.



Heat transfer : Temperature profiles

$$\rho C_p \frac{\partial T}{\partial t} = \nabla (k \nabla T)$$

Required energy for water vaporization at the interface

Boundary Condition at the interface:

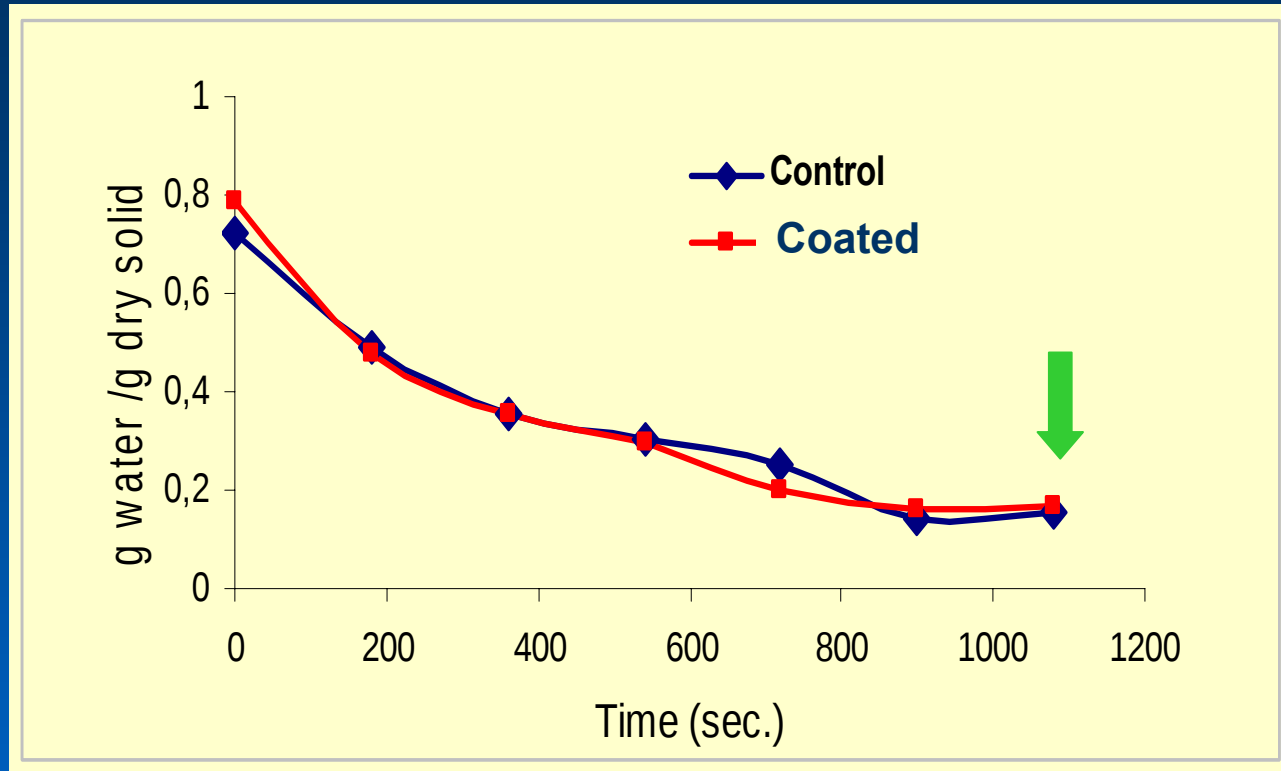
$$x = L \quad -k \frac{\partial T}{\partial x} = h_1 (T - T_{oil}) + L_{vap} m_{vap,1} \quad t > 0$$


Mass Transfer. Water profiles.

$$\frac{\partial C_w}{\partial t} = \nabla (D_w \nabla C_w)$$

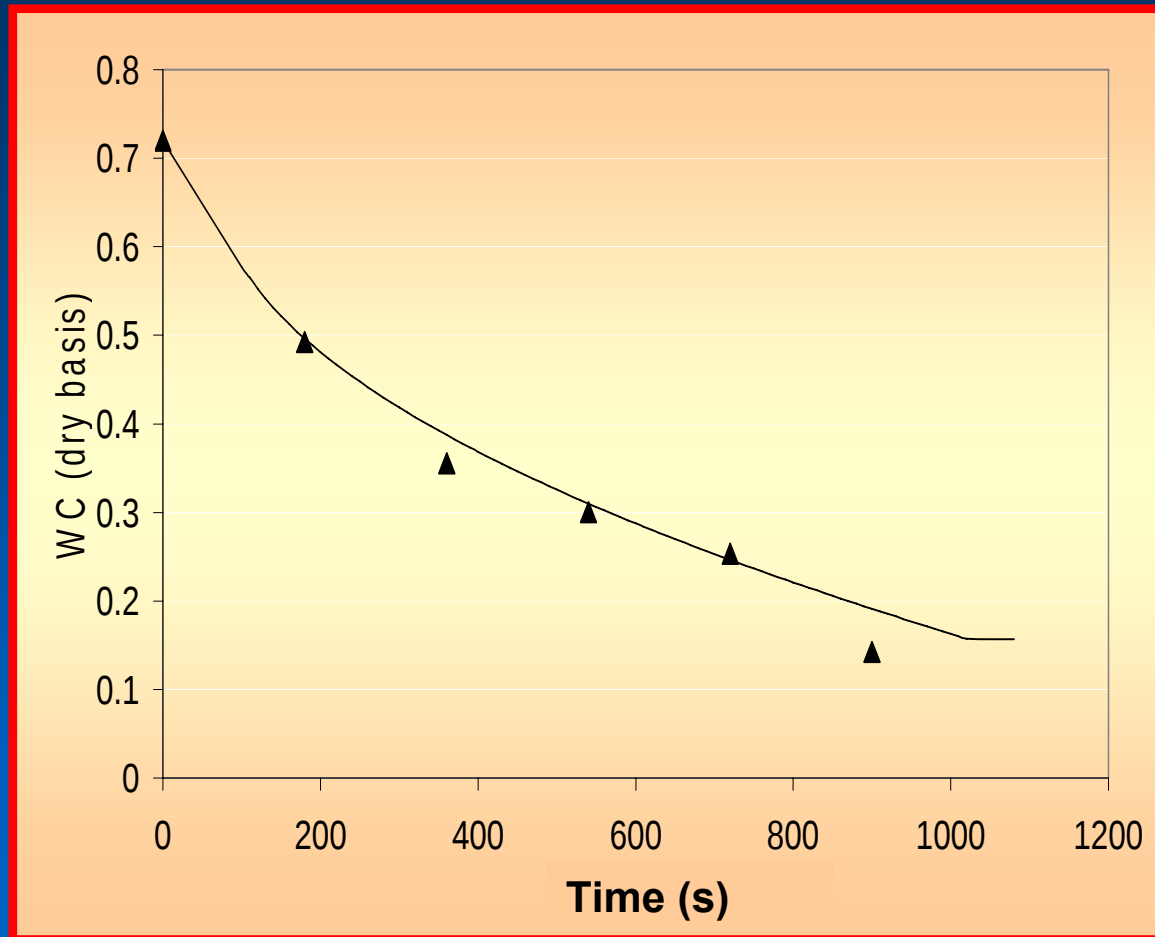
Thermal and physical properties changed with temperature and moisture content. Numerical solution of nonlinear coupled energy and mass transfer partial differential equations, considering a moving boundary was obtained.

Effect of coating on water content



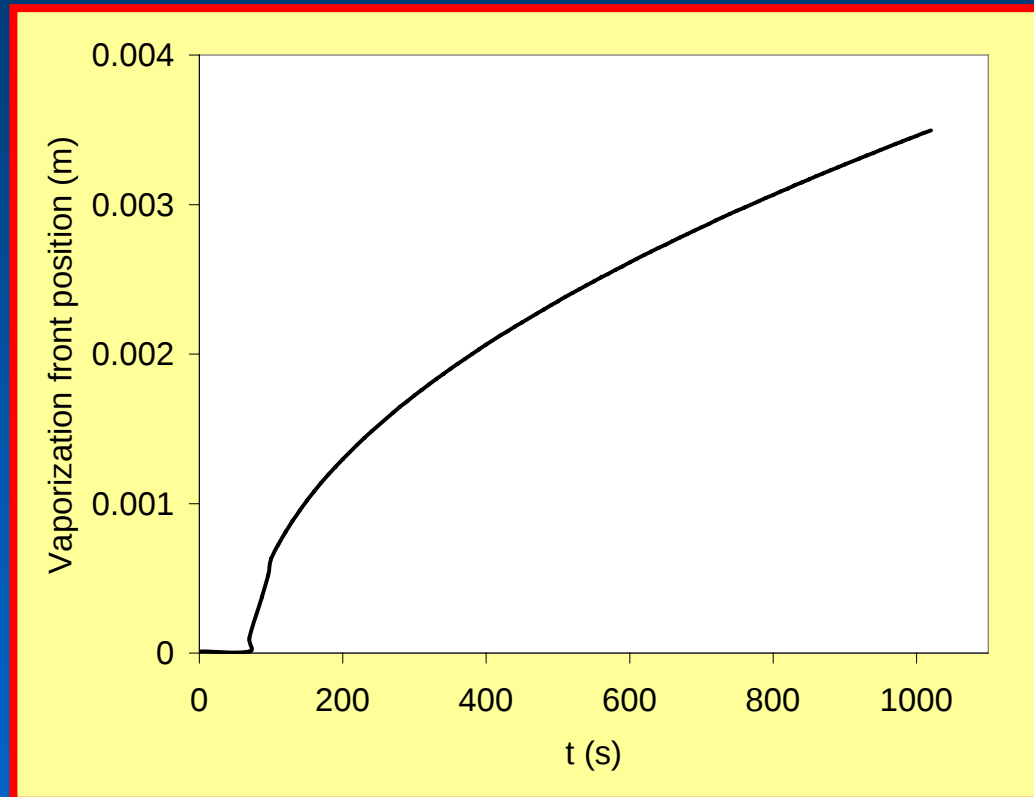
The presence of the coating did not change the moisture content of the samples during frying; this could be attributed to the poor water vapor barrier of MC films, because MC is an hydrophilic polymer.

Water content vs.time



A very good agreement between predicted values by the model and experimental data was observed

The model predicted the position of the vaporization front as a function of frying time

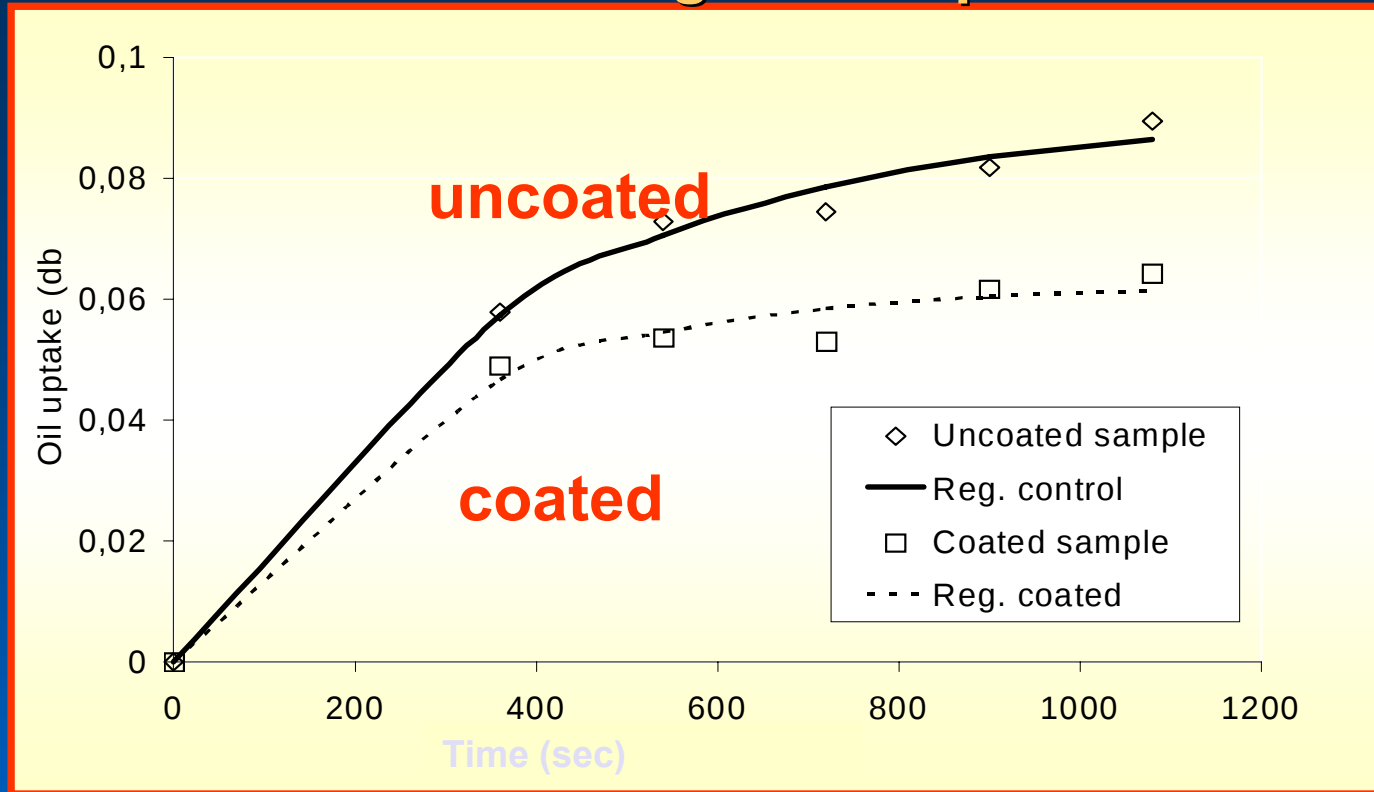


The dehydrated zone thickness (DZ) increases with time

Oil uptake

- During frying the vapor leaves voids for the oil to enter later.
- **Oil uptake (OU) is mainly produced when the product is removed from the frying medium.**
- OU is affected by the microstructure of the dehydrated zone.
- OU depends on the balance between the oil retained on the surface and the oil drained after retrieval of the product from the oil bath.

Effect of the coating on oil uptake

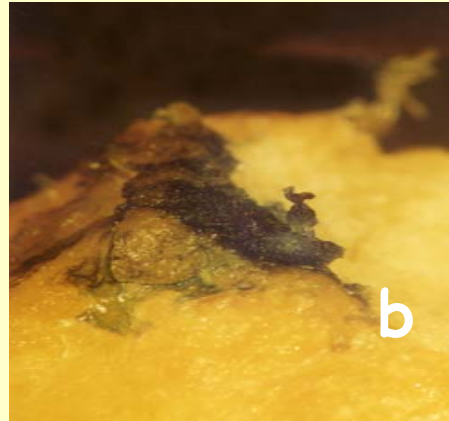
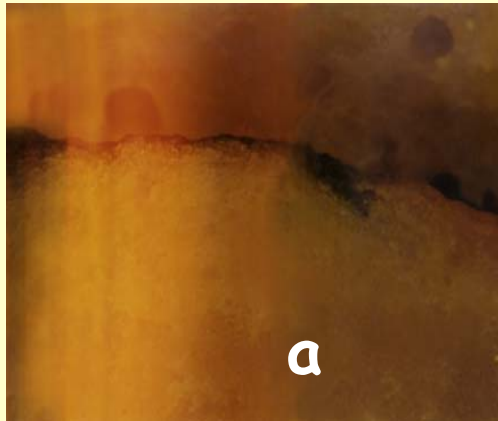


Oil content of coated and uncoated fried dough disc at different frying times.

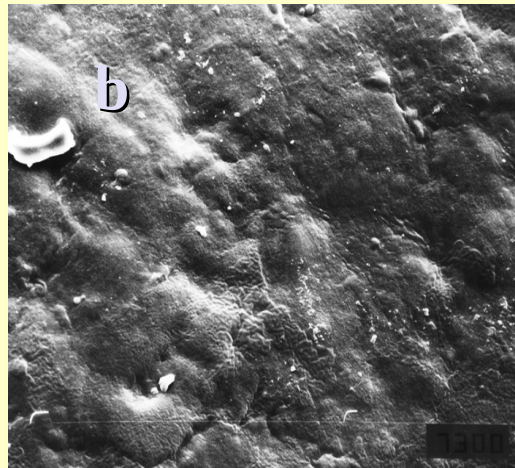
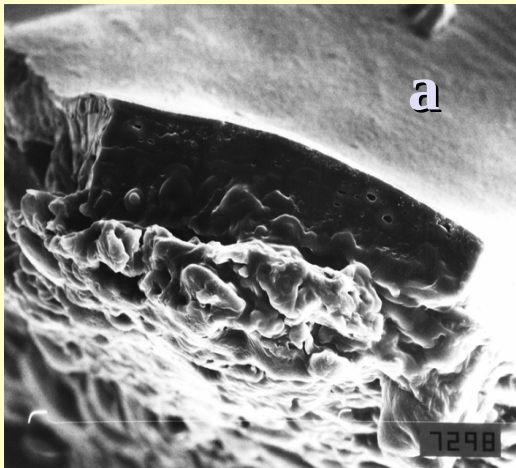
MC coatings reduced the lipid content of the samples; the oil uptake was 30% lower than in uncoated samples.

Microscopic observation of fried samples

Micrographs shows the integrity of the MC layer and the good adhesion of this coating to the fried product.



Light microscopy: (a) cross section (b) surface of a dough disc fried during 12 minutes at 160°C.



SEM micrograph of a) cross section; b) surface of a dough disc submitted to frying

The lower oil uptake in coated samples can be attributed to the presence of the hydrocolloid film MC acting as a lipid barrier, particularly due to its thermal gelation properties.

Quality Attributes: Texture and Color

During the frying process similar values of maximum force and color parameters were obtained for coated and uncoated fried samples.

Sensory analysis: Overall acceptability of coated product was very good.

Panellists could not distinguish between the coated and the uncoated samples.

Other results obtained in our laboratory

Reduction of 40.6 % in the oil content in french fries (0.7 x 0.7x5 cm) using methylcellulose (1%) and sorbitol.

Water content increased: 6.3%

Frying conditions: 4min at 180° C

Non significant differences in surface color and texture



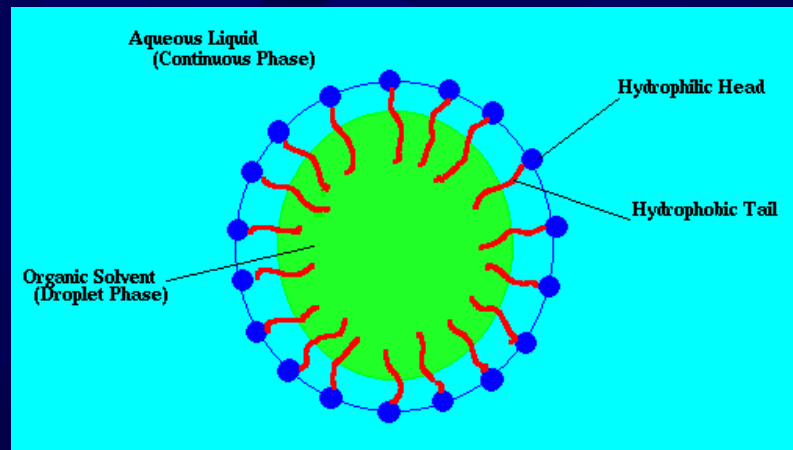
PUBLICATIONS

- Edible coatings from cellulose derivatives to reduce oil uptake in fried products .Garcia, A. Ferrero C., Bertola N. Martino M.and Zaritzky N. *Innovative Food Science and Emerging Technologies* 3, 391-397 (2002) .
- Methylcellulose coating applied to reduce oil uptake in fried products.Garcia M. Ferrero C. Campana A. Bertola N. Martino M. Zaritzky N. *Food Science and Technology International* , 10 (5) 339-346 (2004)
- Comparison of the deep frying process in coated and uncoated dough systems R. Bertolini Suarez, L.A. Campañone, M.A. Garcia, N.E. Zaritzky. *Journal Food Engineering* 84, 383–393.(2008).

RHEOLOGY OF LOW-IN-FAT O/W EMULSIONS

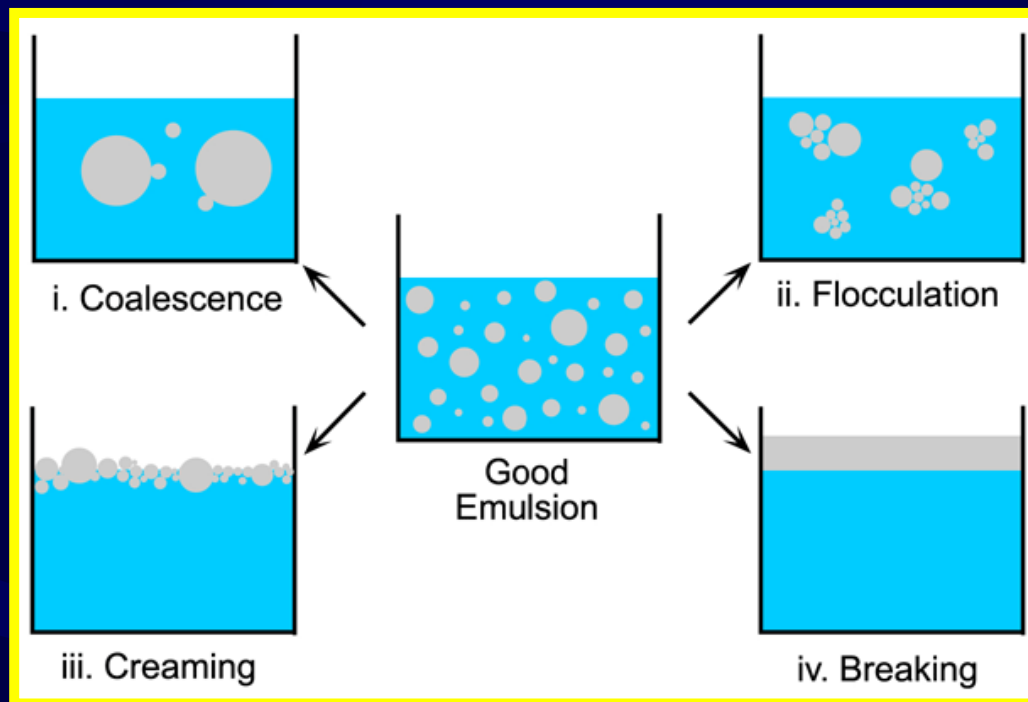
Lorenzo G., Zaritzky N., Califano A.

- ✓ Oil-in-water (O/W) emulsions have attracted considerable attention in the food industry due to their physicochemical properties and physical attributes.
- ✓ Emulsions have a significant potential for the solubilization of active water-insoluble materials, for example food additives such as nutraceuticals or antioxidants.



However, emulsions are thermodynamically unstable systems, **especially those with reduced oil content**, usually splitting into two distinct phases.

The presence of salts and an acidic medium, usually found in several food emulsions enhances the instability of these systems



The addition of a salt to an emulsion alters the colloidal interactions

 **electrostatic repulsion**

 **flocculation**

✓ **Polysaccharides** are usually added to the aqueous phase of low-in-fat o/w food emulsions to improve the stability.

✓ The performance depends on **polymer concentration in the aqueous phase** as well as on the structural features of the aqueous polymer system.

OBJECTIVES

❖ To study the effect of oil and hydrocolloid concentrations on the stability and rheological behavior of :

❖ low-in-fat O/W emulsions

❖ at a low pH

❖ containing salt.

The following systems were analyzed:

❖ **Low-in-fat O/W emulsions**

❖ **Oil** (10 – 30 % wt)

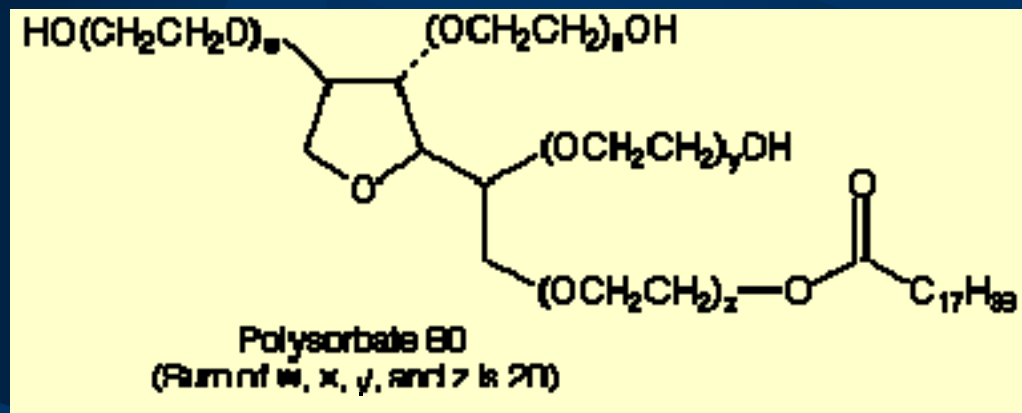
❖ **Hydrocolloids:** xanthan and guar gums (0.5– 2% wt)

❖ **Low pH:** Acetic acid

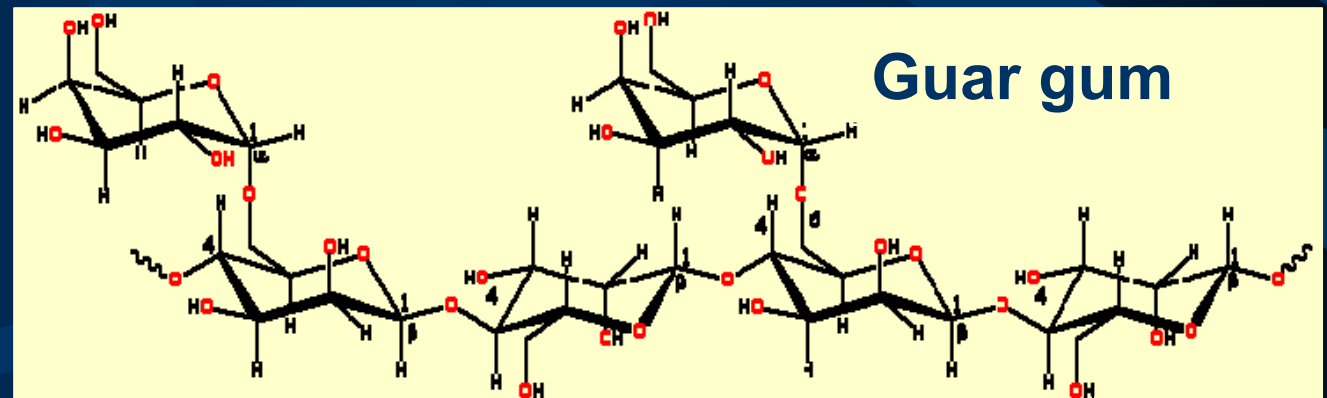
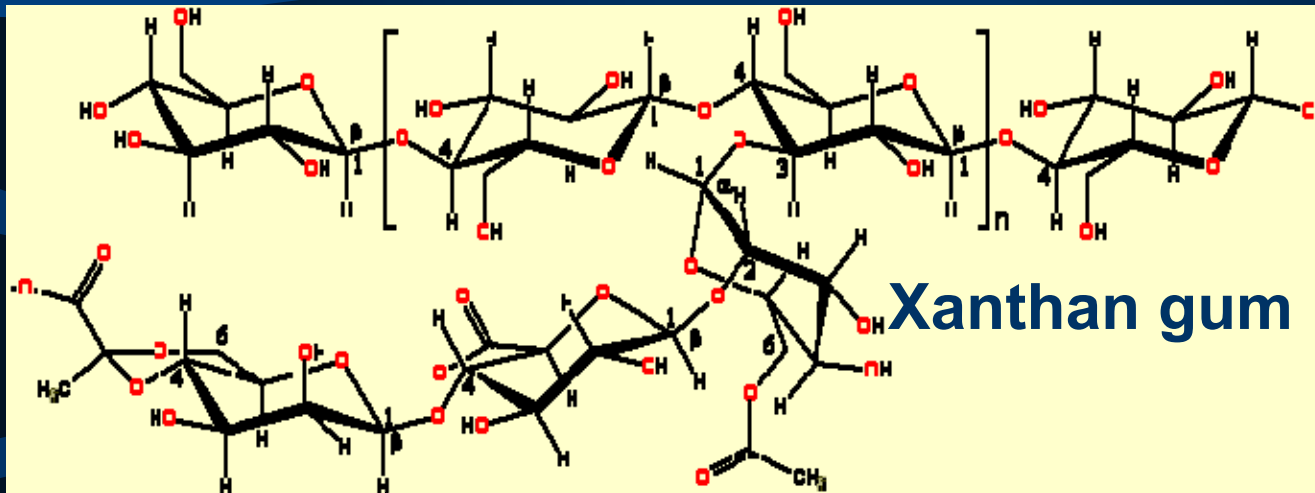
❖ **Salt:** Sodium chloride

Emulsifier: Polyoxyethylene sorbitan monooleate (Tween® 80), Polysorbate 80.

It is one of a series of materials (including Tween 20, 40 and 60) which are **fatty acid esters of sorbitan polyethoxylates**. The various Tweens differ in the type of fatty acid present; Tween 80 is an oleate.



Hydrocolloids : xanthan and guar gums of food-grade commercial type Sigma Chemical Co. (St. Louis, MO).



The effects of oil and hydrocolloid concentrations (xanthan and guar gums) on the stability and rheological behavior of the emulsions were studied by applying the following techniques :

- ✓ Droplet size distribution (DSD)
- ✓ Microscopy observations
- ✓ Stability of the emulsions
- ✓ Rheological behavior of both the continuous phases and the emulsions analyzing:
 - Viscoelastic behavior
 - Steady state flow curves

DROPLET SIZE DISTRIBUTION (DSD)

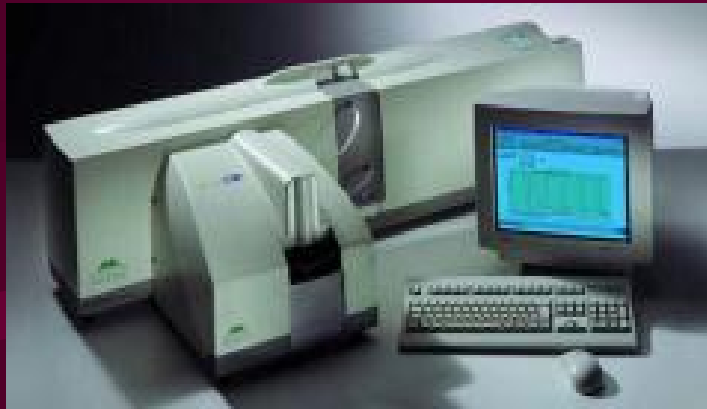
Mean droplet size and droplet size distribution of emulsions were determined by static light scattering using a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, Worcester, UK).

Sauter average diameter $D[3,2]$ was calculated for each sample as follows:

$$D[3,2] = \frac{\sum_{i=1}^N (n_i d_i^3)}{\sum_{i=1}^N (n_i d_i^2)}$$

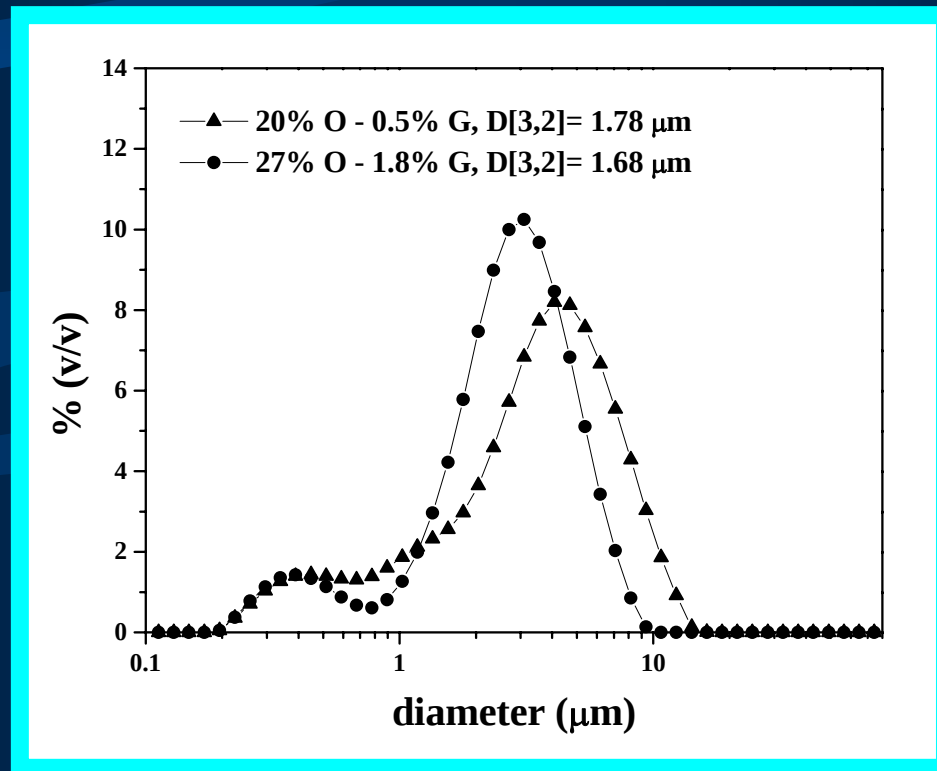
d_i = droplet diameter, N = total number of droplets

n_i = number of droplets having a diameter d_i .



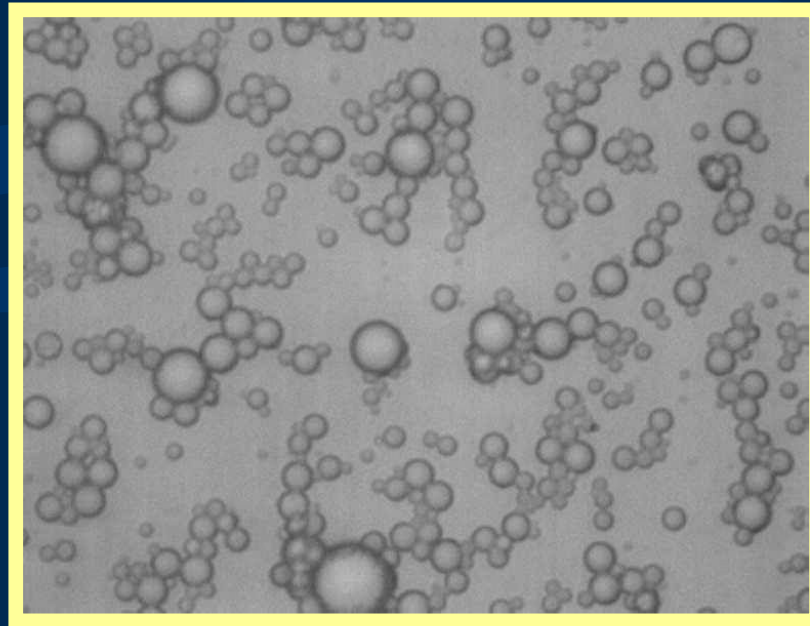
Mastersizer 2000 (Malvern Instruments Ltd., Malvern, Worcester, UK: The diffraction light pattern (He-Ne laser) is dependent on the particle size. The laser diffraction pattern is measured and correlated to the particle size distribution based on Fraunhofer or Mie theory. The use of Mie theory presupposes knowledge of the light refractive index of the particles and the dispersion media and the imaginary part of the refractive index of the particles

By dispersion in an appropriate medium the Malvern Mastersizer 2000, using light scattering technology, measures droplet size in a wide range .



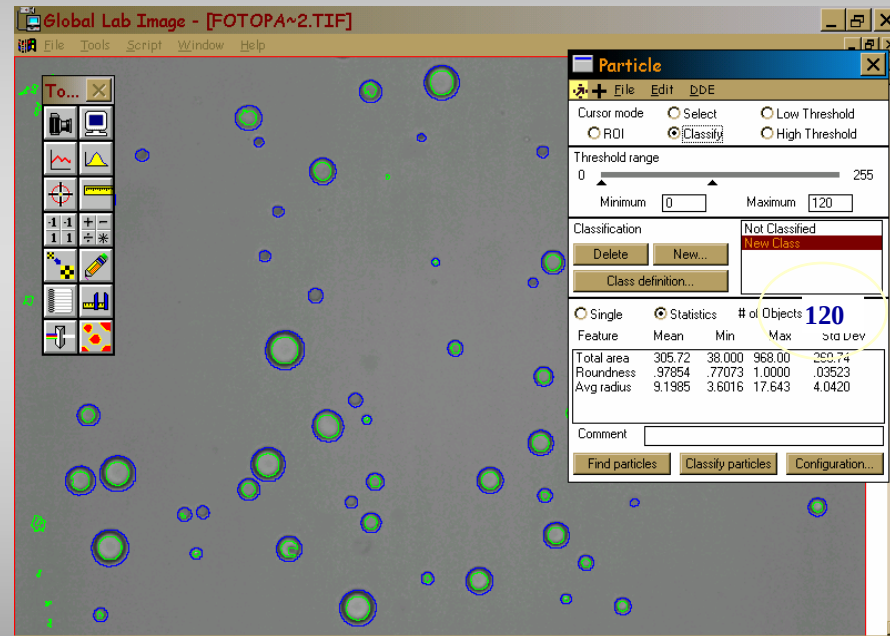
Droplet size distribution was not modified by hydrocolloid content. A bimodal distribution was observed for all the emulsions.

MICROSCOPY OBSERVATIONS of all emulsions were carried out on a microscope coupled to a DC 100 camera (Leica Microscopy Systems Ltd., Heerbrugg, Switzerland)

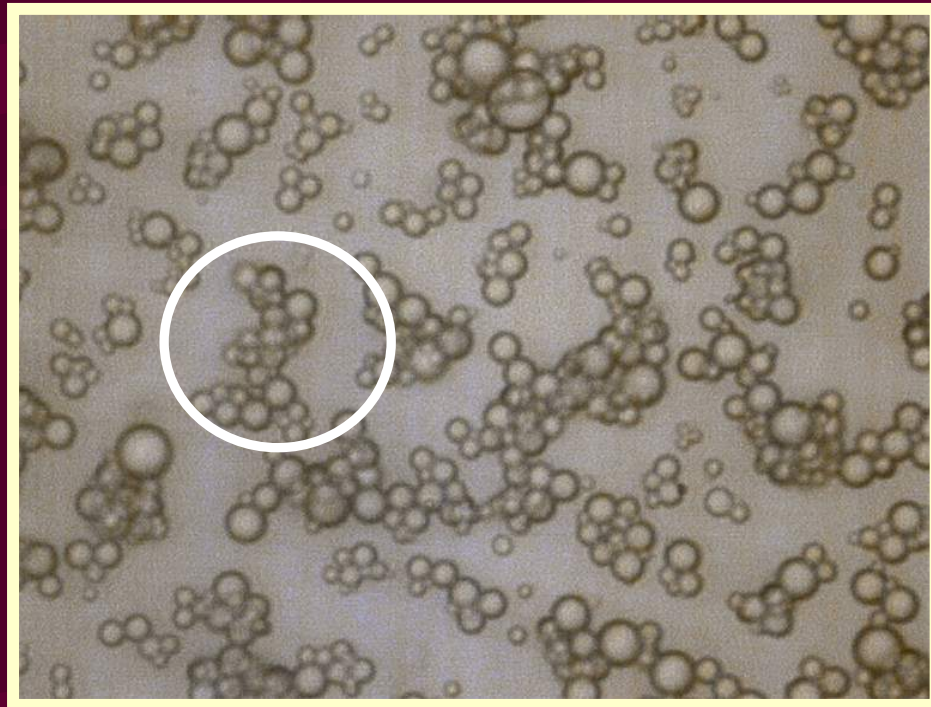


Photomicrograph of o/w emulsion with 20% wt. oil content and a continuous phase containing 0.5% wt. of xanthan-guar mixture.

Light Microscopy associated with image analysis



- ✓ Microscopic observation showed that all the studied emulsions could be considered as **highly flocculated systems**.
- ✓ The micrograph shows an emulsion with clusters of droplets.

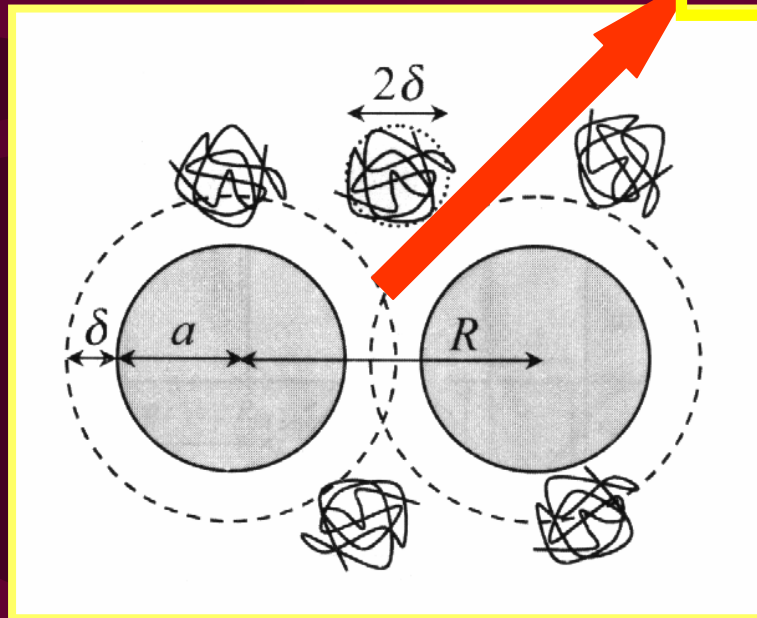


Formulation (20 % O – 1.25% G). 1000x

Depletion flocculation

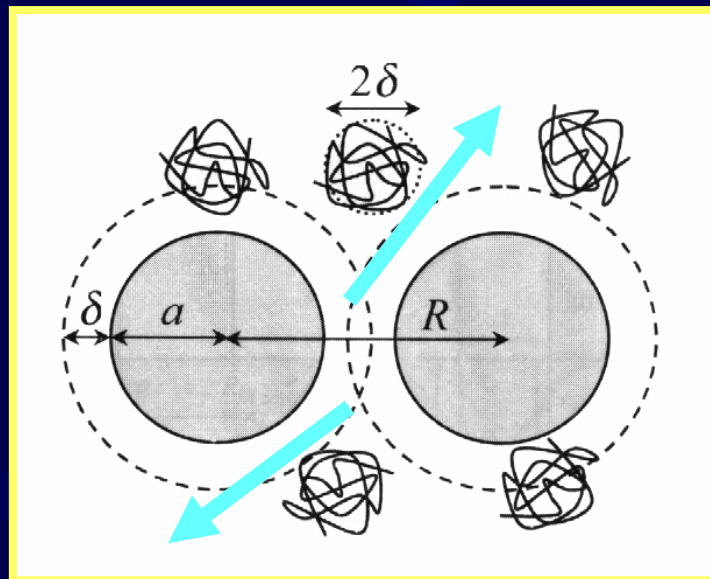
As the droplets came closer together due to Brownian motion, the region between emulsion droplets was depleted of polysaccharides leaving only the solvent.

Polysaccharide
Exclusion zone



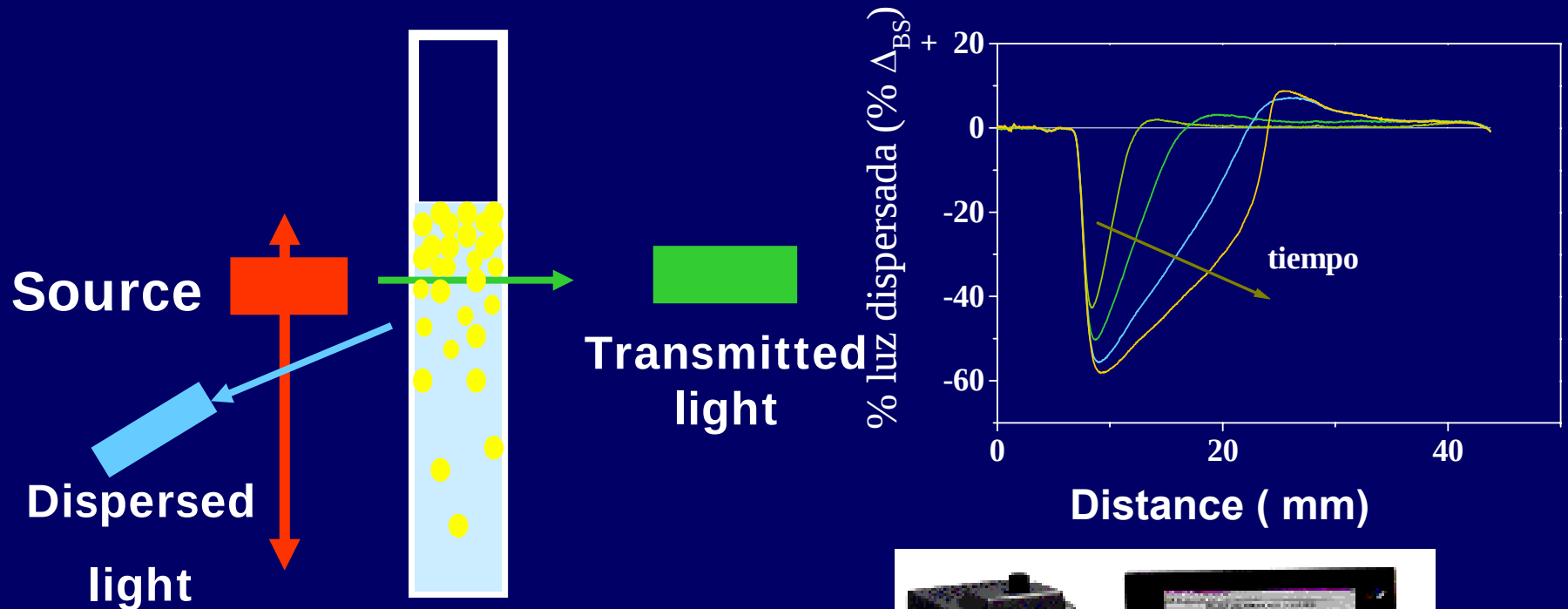
The **depletion of polysaccharides** induced a hydrocolloid concentration gradient between the inter-particle region and the bulk solution.

The **solvent between the droplets tends to diffuse out** to reduce the concentration gradient, **causing the droplets to aggregate**. This phenomenon is known as **depletion-flocculation**



**Solvent
Diffusion**

Emulsion stability was measured using Quick Scan Instrument – Optical method (Beckman-Coulter)



Quintana, Califano, Zaritzky, 2002



✓ All the emulsions studied remained stable for over eight months, even those with the lowest thickening agent content.

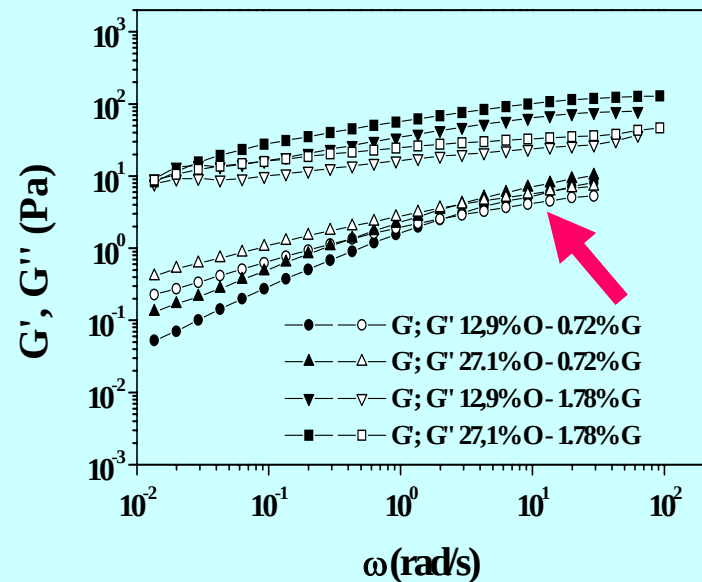
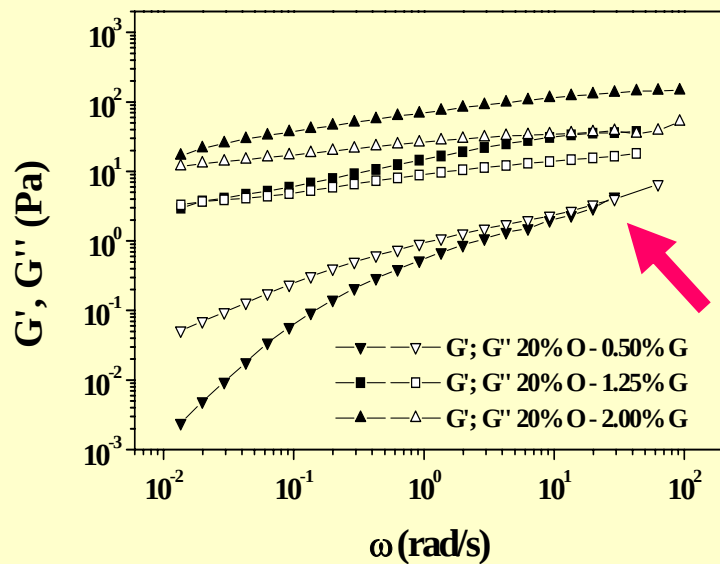
✓ The addition of a xanthan and guar mixture stabilized the emulsion against creaming by increasing the viscosity of the continuous phase as a consequence of a gel network formation

VISCOELASTIC BEHAVIOR OF THE EMULSIONS

- ✓ The mechanical spectra, obtained from small-amplitude oscillatory shear tests, of food emulsions reveal a characteristic dependence on the oil concentration and continuous phase composition.
- ✓ The percentage of hydrocolloids was the major influence on the rheological behavior of the emulsions

Viscoelastic behavior of the emulsions with low hydrocolloid concentrations (0.5 and 0.72%) corresponds to **polymeric solutions**.

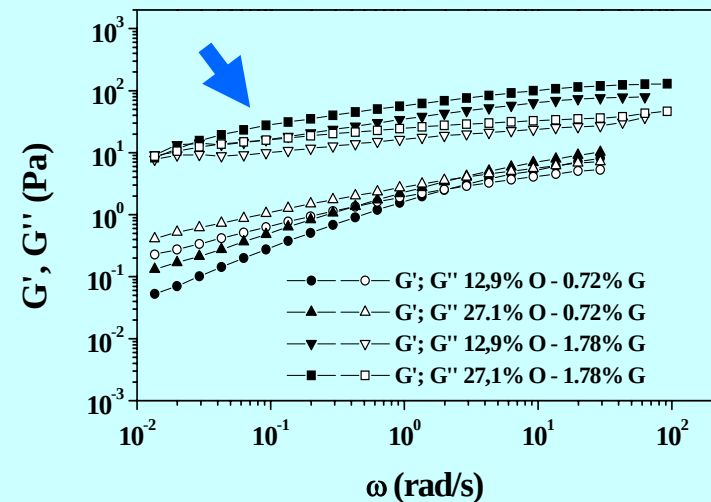
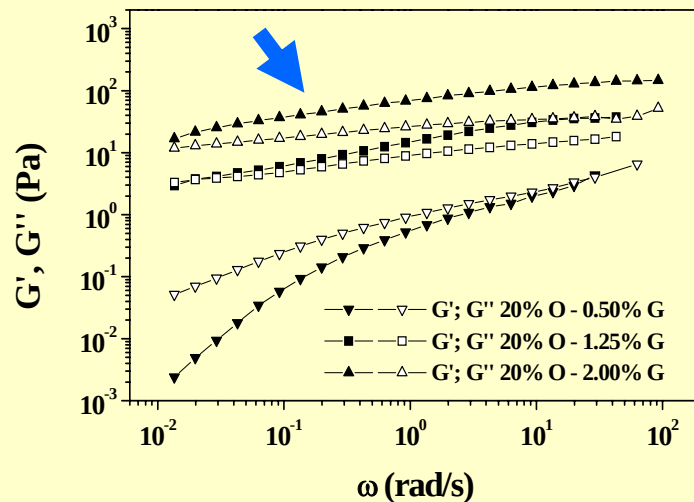
G' and G'' curves intersected within the range of tested frequencies ($\tau \sim 0.1$ s), showing a clear **fluid like behavior**.



When gum concentration was 1.25% or higher, emulsions showed a **weak gel-like behavior** with G' higher than G'' in the analyzed frequency range.

$G < 1.25\% \Rightarrow$ Viscous system ($G'' > G'$)

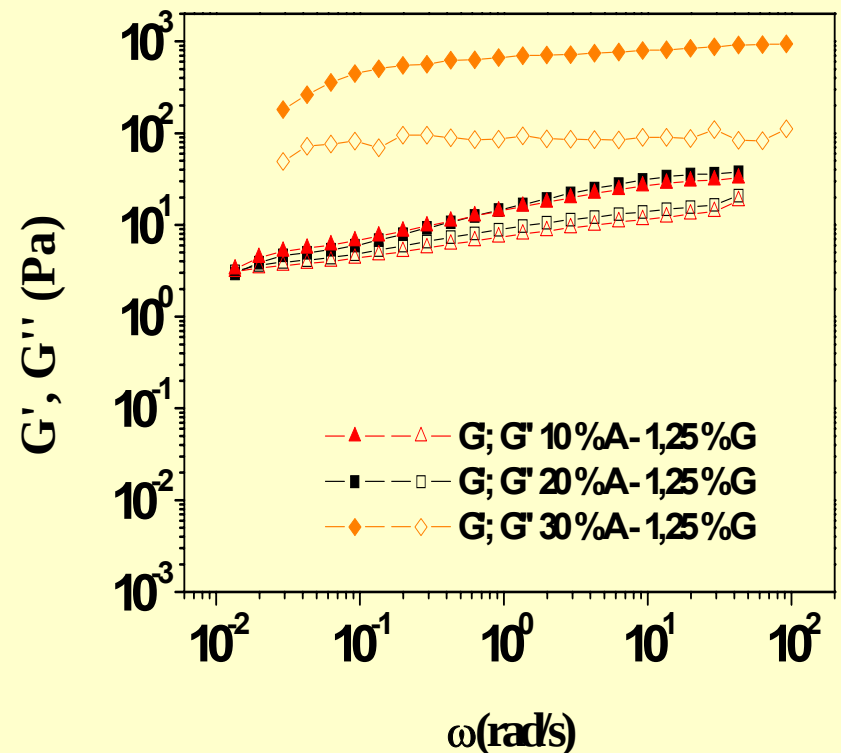
$G \geq 1.25\% \Rightarrow$ Elastic behavior ($G' > G''$)



The emulsion with 30% oil content exhibited an ordered structure, with an elastic modulus independent of the frequency while $G'' < G'$.

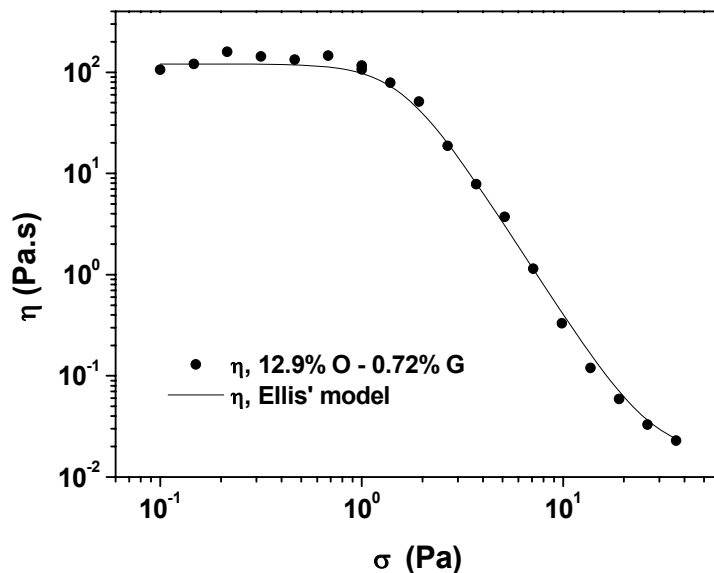
This behavior corresponds to a flocculated system where droplets are forming a structural network

- ❖ Frequency sweeps showed that both G' and G'' increased with oil content.
- ❖ The viscoelastic behavior was mainly governed by the hydrocolloid concentration.



STEADY-STATE FLOW MEASUREMENTS

The steady flow behavior of the emulsions, viscosity (η) vs. shear stress (σ) was studied using a serrated plate- plate geometry (35 mm diameter, 1 mm gap), in order to avoid wall slip phenomena.



Emulsions show a shear-thinning behavior.

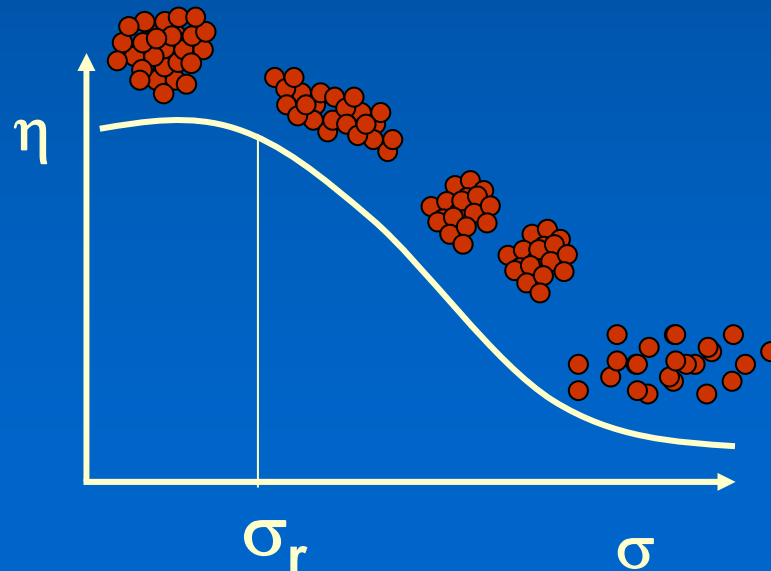
Flow curves correspond to a structured fluid, with well defined regions. At low shear stress (σ), viscosity reaches a limiting value namely zero shear viscosity (η_0) decreasing as the shear stress increases

Steady-state flow curve for food emulsion with 12.9% oil and 0.72% gum content.

Shear-thinning behavior of the emulsions was related to:

- ✓ **Droplet de-flocculation**
- ✓ **Non-Newtonian behavior of the continuous phase.**

The pronounced transition between the second and third region in flocculated emulsions may be attributed to both an irreversible process where shear rate induces changes in droplet size distribution, and a reversible one related to deflocculation



Flow curves were modeled by **Ellis equation** which correlates fluid viscosity with applied shear stress (σ).

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (\sigma / \sigma_c)^n}$$

η_0 and η_{∞} are first and second Newtonian viscosities
 n is the exponent

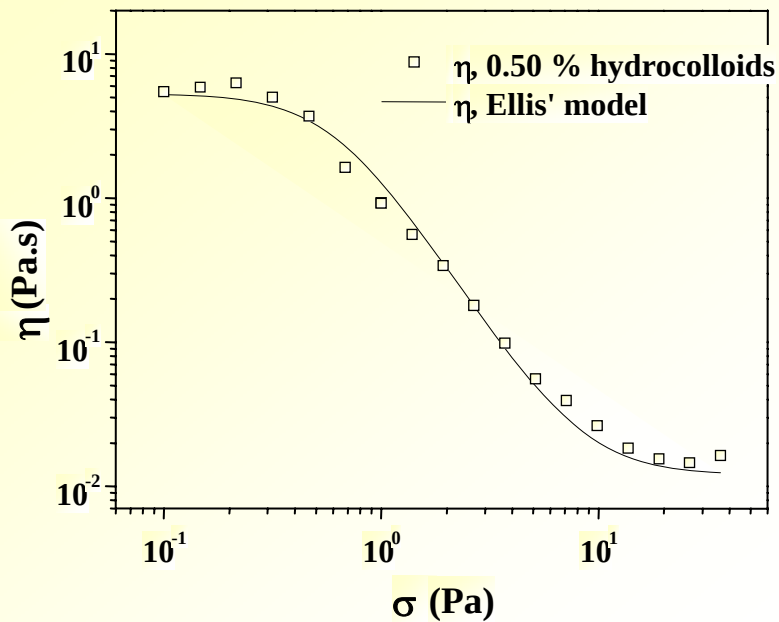
σ_c is a critical stress denoted as “true yield stress” that could be defined as the stress above which the structure of the system is broken down.

Zero shear rate viscosity (η_0) for the continuous aqueous phases and for the emulsions were determined.

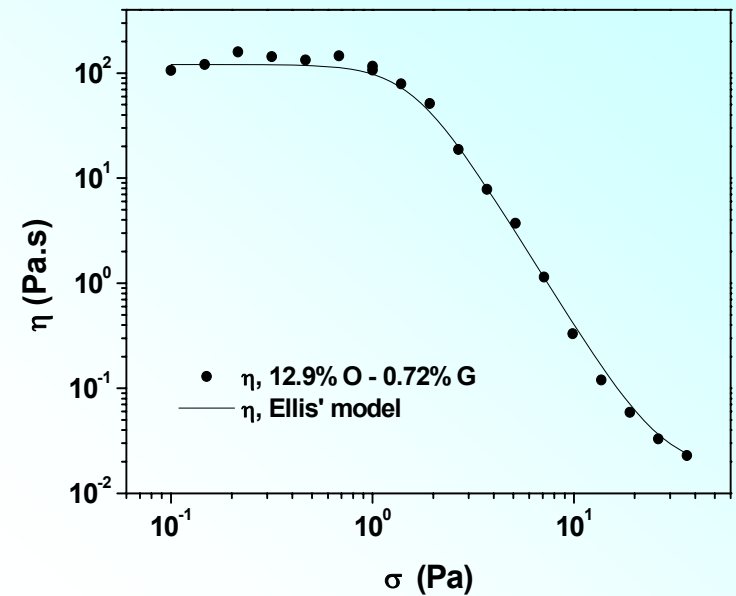
Ellis Model

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (\sigma / \sigma_c)^n}$$

Continuous phase

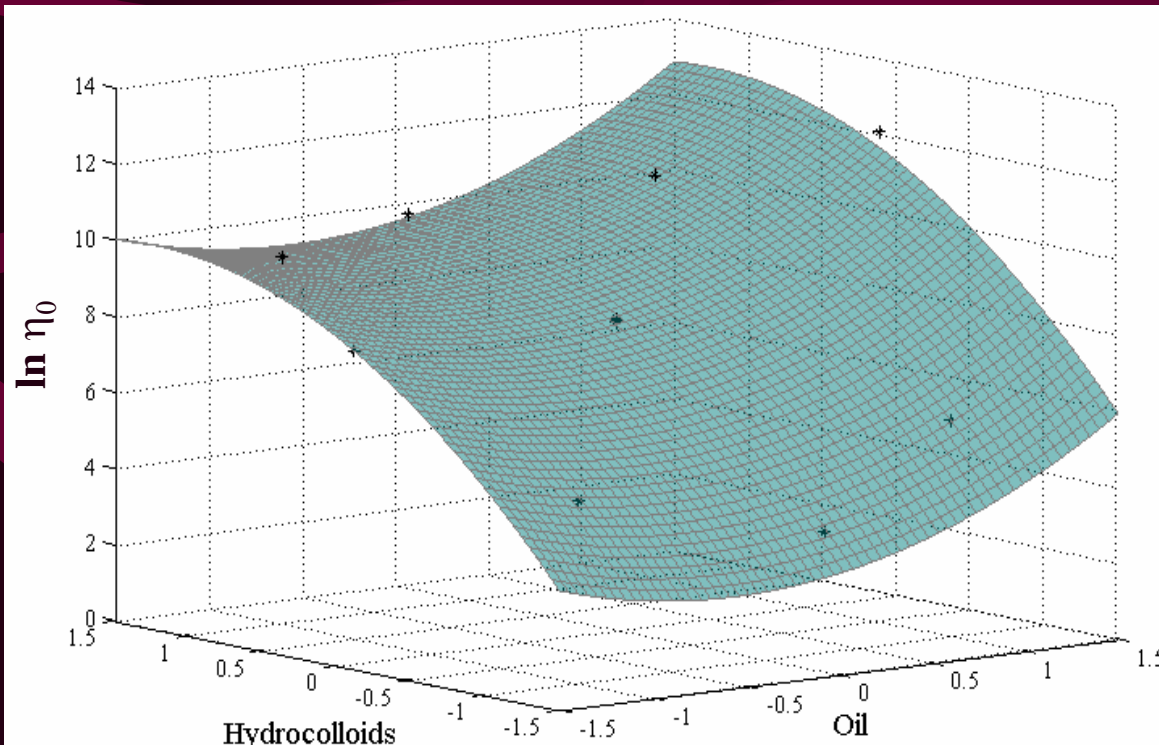


Emulsion



The **response surface methodology** led to a phenomenological equation which allows to predict the necessary hydrocolloids content to develop an emulsion in which oil concentration and viscosity (η_0) are predetermined.

$$\ln(\eta_0) = 8.152 + 0.931 O + 0.83 O^2 + 2.296 G - 0.903 G^2$$



η_0 = zero shear viscosity

Oil: 10 - 30 % wt

Gum: 0.5 – 2% wt

($r = 0.974$)

❖ **Stable low-in-fat o/w emulsions were formulated, with NaCl added and containing acetic acid.**

❖ **Using xanthan – guar mixtures as thickening agents the creaming process was avoided and emulsion stability was ensured for over eight months.**

❖ **The formation of a weak gel-like polymer network in the continuous phase leads to very high viscosities in the low stress range and imparts additional elastic properties to the whole system so that emulsion creaming is strongly inhibited**

PUBLICATIONS

Microstructure and stability of non protein stabilized oil-in-water food emulsions measured by optical methods.

Quintana, J.M., Califano A. and Zaritzky N.

***Journal of Food Science*, 67 (3), 1130-1135, (2002)**

Effect of salt on the rheological properties of low-in-fat O/W emulsions stabilized with polysaccharides.

Quintana, J.M, Califano, A.N., Zaritzky, N.E., Partal, P.

***Food Science and Technology International* .8, (4) 213-222 (2002)**

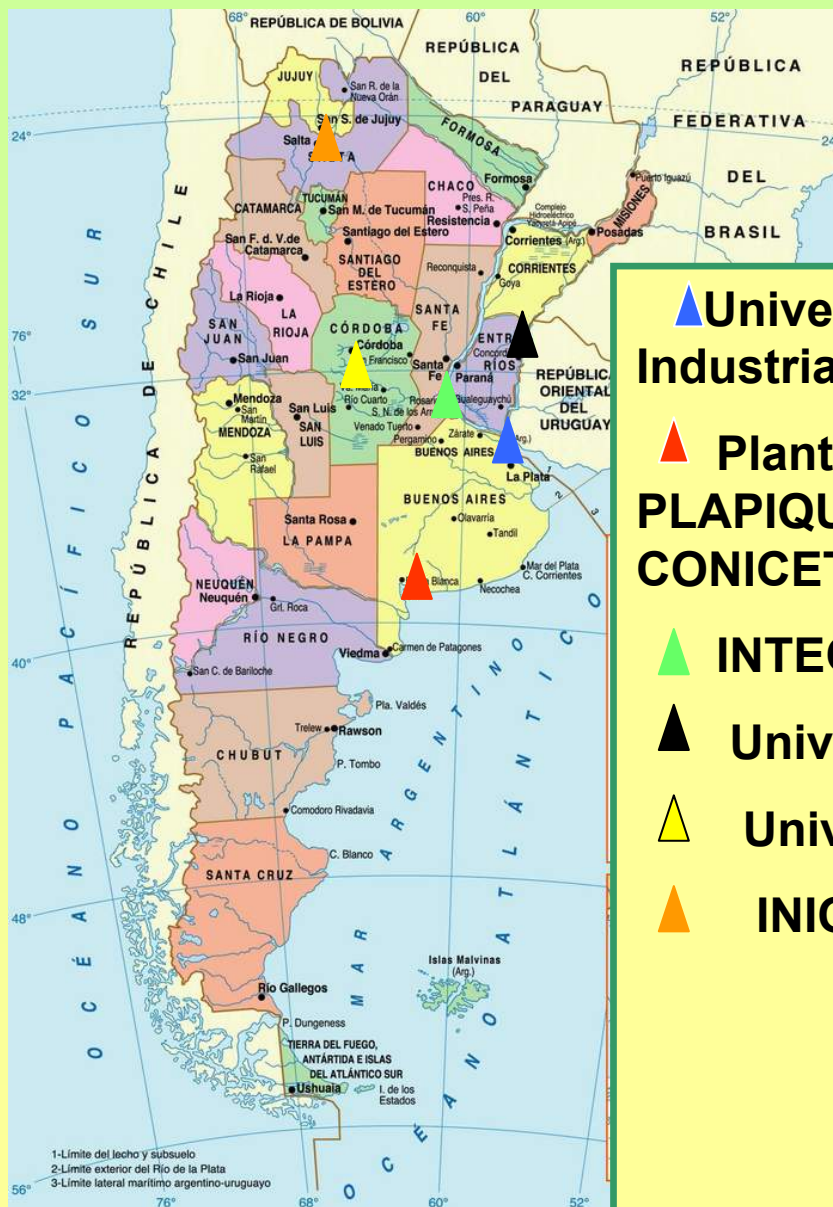
Linear and non linear viscoelastic behavior of oil in water emulsions stabilized with polysaccharides.

Quintana, J.M, Califano, A.N., Zaritzky, N.E., Partal, P.Franco J.M.

***Journal of Texture Studies* 33(3) 215-236 (2002)**

Modeling rheological properties of low-in-fat o/w emulsions stabilized with xanthan/guar mixtures

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