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RHEOLOGICAL PROPERTIES AND MICROSTRUCTURE OF MAIZE STARCH / MILK PROTEINS GELS

Abstract

Maize starch pastes whether containing milk proteins or not behave as shear thinning bodies. The increase in the heating temperature from 100 to 130°C provoked an important decrease in the maize paste viscosity measured at 60°C. The addition of milk proteins greatly changed the effect of heating temperature. A maximum viscosity at 60°C was observed for those pastes heated at 105-115°C for the milk protein concentrate, while for the sodium caseinate it was lowest at 110°C, whereas for the whey protein concentrate, the paste viscosity at 60°C was found to increase during heating.

The maize starch gels revealed two types of structure. In the maize starch gels some regions were composed of spherical particles, others of branched and flat filaments of several μm of length and 0.1 to 0.2 μm thick. The microstructure of mixed gels revealed an independent network for whey and starch fractions. These gels showed intermeshing networks, where each polymer developed its own network and no copolymer structure could be perceived. Sodium caseinate/starch solutions failed to form a continuous network and the gel presented multiple fractures.

Introduction

Over 40 % of starch produced in France is used for food [7]. One of the most important starch applications is in the preparation of milk desserts. Specific interactions between milk proteins and starch can take place during heating. Electrostatic interaction between potato starch and a-casein at pH 4 was shown by the electrolytic conductance method [8]. The viscosity, gelling and thixotropic properties of starch were much reduced in the presence of sodium caseinate [3]. Quite the opposite effect was observed by Lelievre et al. [5]. They found that sodium caseinate increased the viscosity of the starch pastes and a starch – sodium caseinate synergistic effect occurred. Similar results were obtained by Marzin et al. [6].

The aim of this work is to analyse the effects of heating temperature (100–130°C) and milk proteins on the rheological properties and texture of maize starch pastes and gels.

Materials and methods

The following raw materials were used: maize starch (Sigma, Saint Quentin Fallavier, France), low heat milk powder (NIZO, Wageningen, Holland), sodium caseinate and whey protein isolate (Eurial, Herbignac, France). A controlled stress rheometer type Carri-Med CS100 (Rheo, UK) with a cone (4°, 6 cm) and plate geometry was used for rheological measurements.

Two hundred millilitres of water suspensions containing 5 % starch alone or in a mixture with 5 % milk proteins (Nx6.38) were heated during 30 minutes at 100 to 135°C in a small (250 ml) reactor vessel with magnetic stirring. Then the pastes were cooled to 90°C and transferred on to the plate of the rheometer for rheological measurement. For microscopic studies, the gel samples were dehydrated by the Critical Point Drying with CO_2 carried out in an Emscope CPD 750. These were coated with Polaron E5100 and then observed in a JEOL 35 CF Scanning Electron Microscope at 15 kV.

Results and discussion

For all samples analysed, for a shear rate range of 0.1 to 100 s^{-1}, the pastes containing either starch only or starch and milk proteins behaved at 60°C as shear thinning bodies (Fig. 1), with the stress (t) logarithm linearly related to the logarithm of the shear rate (g):

$$Log(t) = Log(K) + n \, Log(g) \tag{1}$$

where: K – consistency index or the stress level (in Pa) for g = 1 s^{-1} and n – structure or behaviour index.

For the pastes composed of the maize starch only, the logarithm of the shear stress was found to decrease with pasting temperature (Fig. 1A), following the Arrhenius type relation:

$$Log(t) = A + E / RT \tag{2}$$

where: A – hypothetical stress level for T – infinity, E – activation energy of flow (in J/mol), R – gas constant = 8.314 J/mol K, T – absolute temperature (K).

The maize starch / whey proteins pastes (Fig. 1B) increased their strength as the pasting temperature rose. Those pastes prepared from maize starch and the milk powder (Fig. 1C) showed a maximum stress level for pasting temperatures between 110 and 115°C. On the other hand, the pastes containing sodium caseinate (Fig. 1D) were 4 to 6 times softer at 60°C than all other pastes and they presented a minimum stress for at a pasting temperature of 110°C.

A lower viscosity in starch / sodium caseinate pastes heated at 90°C was observed by Hermansson [3]. The opposite tendency was observed by Lelievre et al. [5],
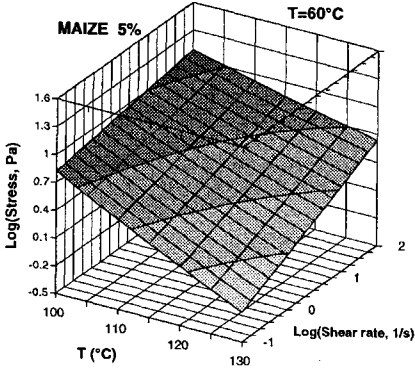
and Marzin et al. [6]. The reason for these differences could be the different sources of sodium caseinate and its composition [3]. The important differences in rheological behaviour of starch/protein pastes between the sodium caseinate and the milk protein, composed of 80 % of casein, might be the different structure of casein in milk and sodium caseinate. In absence of calcium in the sodium caseinate, the casein fractions (α-, β-, κ-) form oligomeres of a low degree of aggregation. These can interact with starch polysaccharides (amylose and amylopectine), by forming phosphate – hydrogen bridges. Thus associated polysaccharide – casein molecules became negatively charged at pH > 4.6 and would not aggregate any further. This could explain the important decrease in the paste viscosity in the presence of sodium caseinate within the heating temperature range of 100 to 110°C (Fig. 1D). Heating during half an hour at over 110°C might cause inter – molecular, protein – protein or protein – polysaccharide cross-linkage reactions between some reactive side groups of amino acids and sugars. These results in the viscosity increase of the pastes for heating temperature above 110°C (Fig. 1D).

In milk, in the presence of calcium, the casein fractions are aggregated into micelles made up of 105–107 molecules of caseins (α-, β- and κ-). The micellar casein has no "reactive" phosphate groups and because of the enormous "molecular / micellar " weight (~109 daltons) its reactivity is next to none. This would explain the differences in the rheological properties between the starch / milk proteins and the starch / sodium caseinate pastes (Fig. 1C and 1D).
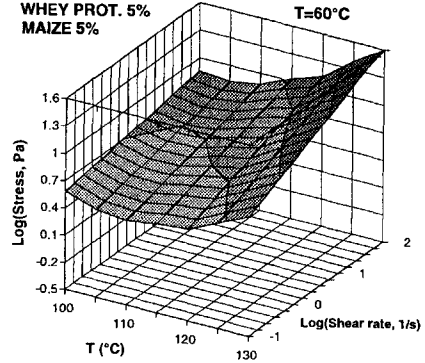
Whey proteins (β-lactoglobulin, α-lactalbumin and serum albumin) are heat coagulating proteins and precipitate when heated above 70°C. The strength of the gel formed is a function of the degree of protein coagulation, being related to the heating temperature. This could explain the continuous increase in the viscosity of the starch / whey proteins pastes (Fig. 1B).

As typical of for the thixotropic products, the level of the consistency index (K) from the equation (1) was higher for the increasing than for the decreasing shear rate (Fig. 2A). It was lower for the second and third shearing cycle. This difference was more pronounced for the increasing than for the decreasing shear rate The addition of sodium caseinate provoked an important decrease in the consistency index if compared with the paste containing only starch. On the other hand, those pastes containing starch and whey proteins were about twice as viscous and much less thixotropic than samples of starch only paste. The addition of milk induced only minimal changes in the consistency index at 60°C but at 25°C it was much higher than at 60°C (Fig. 2B). This is due to the gelation process taking place during cooling. The greatest increase in the consistency index was observed for the starch / milk gels and the least for the starch / sodium caseinate pastes.
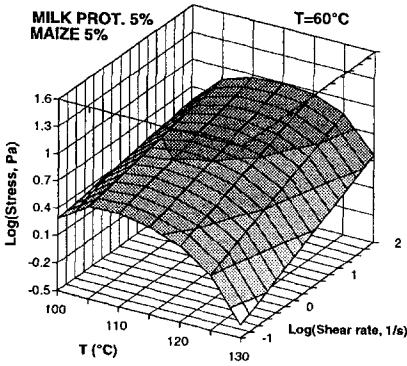
A

MAIZE 5%   T=60°C

B

WHEY PROT. 5%   T=60°C
MAIZE 5%

C

MILK PROT. 5%   T=60°C
MAIZE 5%

D

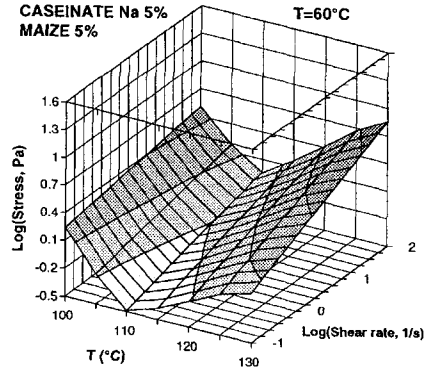CASEINATE Na 5%   T=60°C
MAIZE 5%

Fig. 1. Logarithm of the shearing stress as a function of the pasting temperature and the logarithm of the
shear rate at 60°C for the 5 % maize starch only (A) and when mixed with: whey protein isolate
(B), milk proteins (C) and sodium caseinate (D).
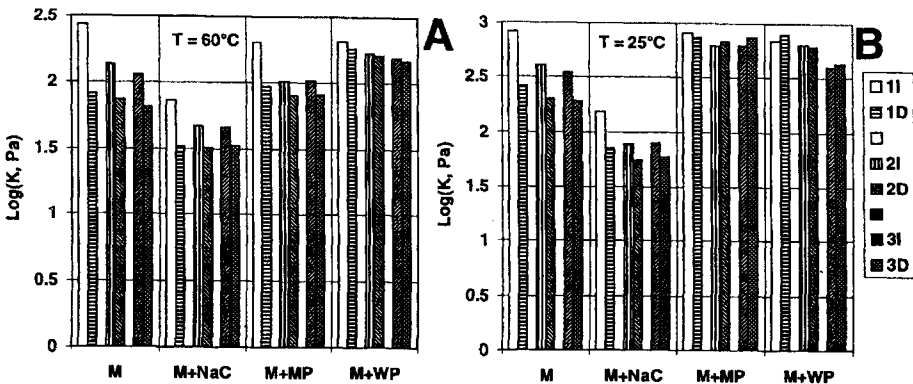
A   T = 60°C

B   T = 25°C

Fig. 2. Logarithm of the consistency index (K) at 60°C (A) and 25°C (B) for the pastes and gels of 5 %
maize starch only (M) and when mixed with: sodium caseinate (NaC), milk proteins (MP) and
whey proteins (WP) for the first three shearing cycles (1, 2, 3) for the increasing (I) and decreas-
ing (D) shear rate.

The structure index (n) from equation (1) varied between 0.15 and 0.48 (Fig. 3). It was on average about 0.1 lower for the increasing shear rate. This is typical thixotropic behaviour. The structure index was slightly higher at 25°C for starch alone and starch/sodium caseinate pastes and slightly lower for the starch/milk and the starch/whey protein pastes. The structure index is equal to 1 for Newtonian bodies and is below 1 for so called shear thinning bodies. A similar level of the structure index (0.4 < n < 0.6) we observed previously for starch pastes heated at the temperatures < 100°C [4].
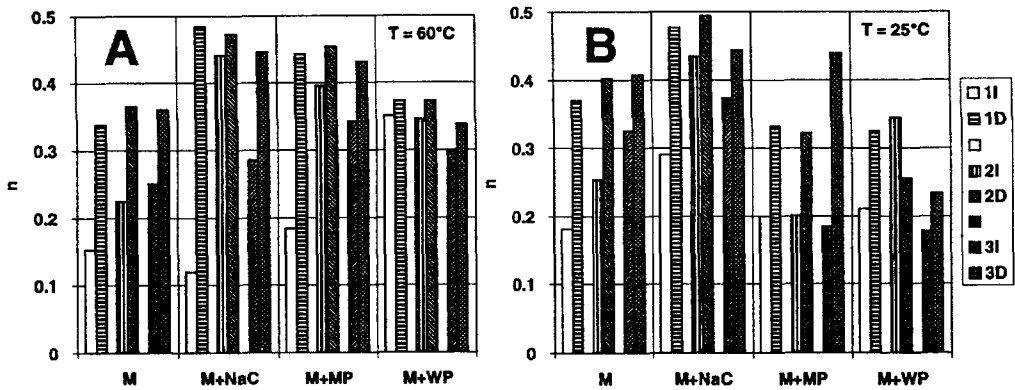

Fig. 3.   Structure index (n) at 60°C (A) and 25°C (B) for the pastes and gels of the 5% maize starch only (M) and when mixed with: sodium caseinate (NaC), milk proteins (MP) and whey proteins (WP) for the first three shearing cycles (1, 2, 3) for the increasing (I) and decreasing (D) shear rate.

The activation energy of flow (E from the equation 2) varied between 5 and 20 kJ/mol depending on the composition of the paste (Fig. 4). It was lowest for the starch/sodium caseinate and highest for the starch/milk pastes. The activation energy of flow corresponds to structural changes during cooling between 60 and 25°C. This confirms the inhibiting effect of sodium caseinate on the retrogradation process.

As typical of thixotropic materials [2], there was a significant difference between the stress evolution of the increasing and that of the decreasing shear rate (Fig. 5). Stress decrease during shearing can be explained by a decrease in the extent of aggregation of the gel particles. These are also capable of assuming some structural reformation by flocculation. The thixotropic behaviour of both pastes and gels suggests that under continuous shear there is a continuous process of destruction/restoration of intermolecular linkages. This is a function of the product composition and structure, of the shearing time and of the shear rate and can be measured using the viscometric method. The thixotropy can be quantified as an absolute or a relative area of the hysteresis loop, between their values for the increasing and decreasing shear rate.
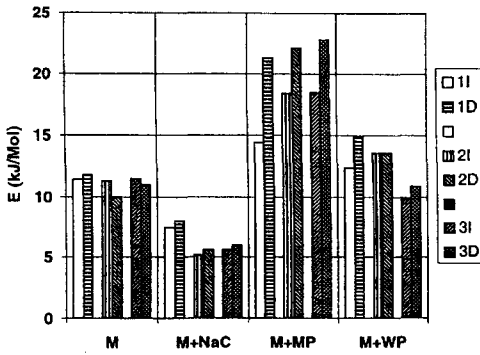
Fig. 4. Activation energy of flow (E) for the pastes and gels containing 5% maize starch only (M) and when mixed with: sodium caseinate (NaC), milk proteins (MP) and whey proteins (WP) for the first three shearing cycles (1, 2, 3) for the increasing (I) and decreasing (D) shear rate.
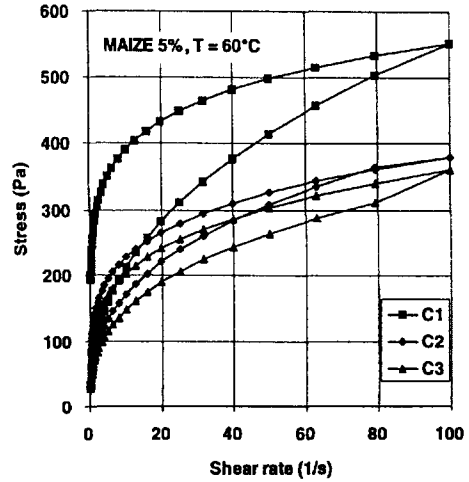
Fig. 5. Stress evolution at 60°C during the first three cycles of shearing (C1, C2, C3), for the 5% maize starch paste, for the increasing and decreasing shear rate.
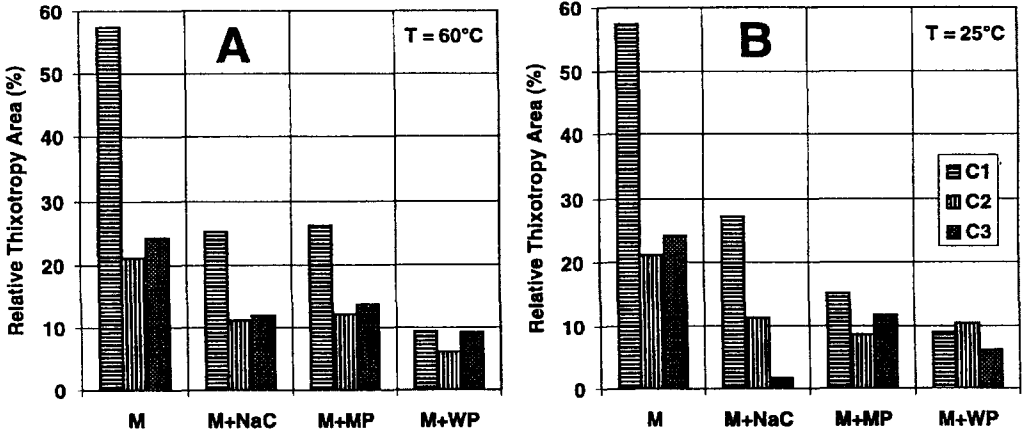

Fig. 6. Relative thixotropic area at 60°C (A) and 25°C (B) for pastes and gels containing 5% maize starch only (M) and when mixed with: sodium caseinate (NaC), milk proteins (MP) and whey proteins (WP) for the first three shearing cycles (C1, C2, C3).

The thixotropic properties of the starch/milk protein mixtures were much lower than of the starch only pastes and gels (Fig. 6). For the starch alone, the relative area of the thixotropic loop represented over 50 % of the total surface under the viscosity versus shear rate curve, for the first shearing cycle. For the second and third shearing cycles it represented only about 20 % for the starch only pastes and gels and about 10 % for the starch/milk proteins mixtures. This means that the addition of the milk proteins greatly changes of the structure of the resulting pastes and gels.
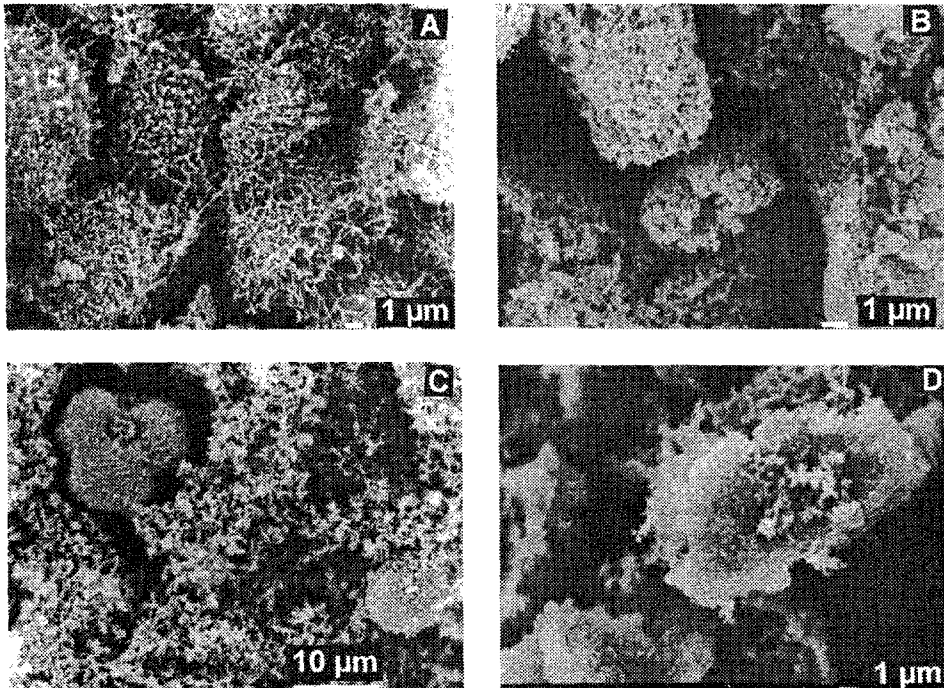

Fig. 7. Scanning electron micrographs of gels containing 5% maize starch only (A) and when mixed with: sodium caseinate (B), whey proteins (C) and milk proteins (D).

The starch only gel is made up of swollen starch granules having a filamentous structure, interconnected by a network of filaments 0.1–0.2 μm thick and several μm long (Fig. 7A). In the presence of the sodium caseinate (Fig. 7B) the swollen grain structure is no longer filamentous but granular and no intergrain filaments are observed. It is possible that the sodium caseinate sticks to the surface of the starch grains and inhibits the departure of amylose from the grains and prevents from forming the filamentous structure [6]. In the whey proteins/maize starch gel (Fig. 7C) the swollen starch grains are embedded in the continuous phase which is composed of irregular aggregates of coagulated whey proteins of variable dimensions. No interpenetration

between the protein and starch networks was observed. Similar results were obtained for manioc starch/whey proteins gels [1]. Mostly granular, similar to sodium caseinate (Fig. 7B) gels, but also partly filamentous structure is observed in the maize starch / milk protein gels (7D).

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REOLOGICZNE WŁAŚCIWOŚCI I MIKROSTRUKTURA ŻELI ZE SKROBI KUKURYDZIANEJ I BIAŁEK MLEKA

S t r e s z c z e n i e

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Celem pracy było zbadanie wpływu temperatury obróbki cieplnej (100 < T_{oc} < 130, 30 minut) w trakcie żelatynizacji kleików ze skrobi kukurydzianej (C = 5 % w/w) i dodatku (5 %) białek mlecznych (pełne białko mleka, kazeinian sodowy, izolat białka serwatkowego) na lepkość (w zakresie prędkości ścinania od 0.1 do 100 s^{-1}), własności tiksotropowe kleików w temperaturze 60°C i 25°C oraz na strukturę mikroskopową otrzymanych z nich żeli.

Lepkość kleików ze skrobi kukurydzianej (5 %) z dodatkiem (5 %) lub bez dodatku białek mlecznych spada ze wzrostem prędkości ścinania. Zwiększenie T_{oc} ze 100°C do 130°C powoduje bardzo istotną obniżkę lepkości kleików mierzonej w temperaturze 60°C. Kleiki skrobiowe z dodatkiem 5% pełnego białka mlecznego wykazywały maksymalną lepkość dla T_{oc} = 105°C do 115°C. Natomiast z dodatkiem kazeinianu sodu wykazywały one minimalną lepkość przy T_{oc} = 110°C. Przy dodatku białek serwatkowych lepkość zwiększała się wraz ze wzrostem T_{oc}. Najwyższe własności tiksotropowe wykazywały kleiki skrobiowe bez dodatku białek mlecznych zaś najniższe z dodatkiem kazeinianu sodu.

Żel ze skrobi kukurydzianej jest zbudowany z napęczniałych ziarenek (10–30 μm) charakteryzujących się strukturą włóknistą. Włókienka o grubości 0.1–0.2 μm zbudowane prawdopodobnie z amylozy mają długość rzędu kilkunasu do kilkudziesięciu μm i łączą sąsiadujące ziarenka skrobi. Przy dodatku kazeinianu sodu struktura ziarenek staje się gąbczasta oraz znikają połączenia międzyziarnowe. W żelu z dodatkiem białek serwatkowych ziarenka skrobiowe są zatopione w gąbczastej strukturze skoagulowanego białka.