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## EFFECT OF HEAT TREATMENT ON THE RHEOLOGY AND MICROSTRUCTURE OF MAIZE STARCH GELS

### Abstract

The normal and waxy maize starch pastes presented at 60°C a shear thinning, power law type behaviour, with the consistency index decreasing with the rise of the pasting temperature from 100 to 130°C. The structure index, for both types of pastes was on average about 0.4 and it was only slightly increasing when the pasting temperature rose. The maize starch pastes presented much greater thixotropic properties than did the waxy starch pastes. The gelation at 25°C followed the kinetic of the first order reaction. The reaction rate constant was about 10 times lower for the waxy than for the normal maize starch gels. The maize starch gels have the filamentous structure, while the waxy starch gels are composed of grapes of small (0.1 µm), roughly spherical particles.

### Introduction

The main reason for using starch and its derivatives as additives in food preparation is to retain water and to increase the product viscosity. Native starch granules have semicrystalline structure and contain about 10-20% water [7, 17, 20-23, 31-32, 39-41]. At low water content (<1.5%) the crystalline structure remains unchanged even after high temperature (232°C) treatment [7]. While heated in presence of excess water, water, above so called gelatinization temperature the starch granules loose their crystalline structure. They are swelling and retain up to 80 g of water per gram of dry matter depending mainly on the starch species [2-4, 5-13, 26, 29, 32]. A part of starch (mainly amylose) is solubilized during the gelatinization process [14-15, 19, 24-26, 33-34]. During cooling and storage the solubilized and hydrated amylose and amylopectin either precipitate (at low concentrations) or form a gel [1-2, 9-10, 12, 16-18, 27-30, 33-38] and eventually partly recrystallize [32, 35].

The aim of this work was to study the effect of heating at temperatures over 100°C on the rheological properties and the microstructure of the normal and waxy maize starch gels.

## Materials and methods

The following raw materials were used: maize starch and waxy starch (Sigma, Saint Quentin Fallavier, 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 4% or 5% starch were heated during 30 minutes at 100 to 135°C in a small (250 ml) stainless steel reactor vessel with magnetic stirring. Then the pastes were cooled to 90°C and transferred on the plate of the rheometer for rheological measurement. For microscopic studies the gel samples were prepared from the starch suspensions containing 10% of normal or waxy starch. They were heated at 110°C during 30 minutes then cooled to 25°C. The heating and cooling rate was 1°C/min. After cooling the samples were left overnight at room temperature. Then they were dehydrated by the Critical Point Drying with CO<sub>2</sub>, carried out in an Emscope CPD 75, coated with Polaron E5 100 and then observed in a JEOL 35 CF Scanning Electron Microscope at 5 to 15 kV.

## Results and discussion

All analysed samples (Fig. 1) show shear thinning behaviour, with the logarithm of the apparent viscosity ( $\eta_a$  in Pa·s) being proportional to the logarithm of the shear rate ( $\dot{\gamma}$  in s<sup>-1</sup>):

$$\text{Log}(\eta_a) = K + (n - 1) \text{Log}(\dot{\gamma}) \quad (1)$$

where: K = consistency index or the logarithm of the apparent viscosity for the shear rate  $\dot{\gamma} = 1 \text{ s}^{-1}$ , n – structure or behaviour index.

The consistency index (K) decreases with the increase in pasting temperature, following the Arrhenius type relation:

$$K = A + E/RT \quad (2)$$

where: A = hypothetical apparent viscosity level for T = infinity and  $\dot{\gamma} = 1 \text{ s}^{-1}$ , E = activation energy of flow in J/mol, R – gas constant = 8.314 J/mol<sup>-1</sup> · K<sup>-1</sup>, T = absolute temperature (K).

With the increase of the pasting temperature, the apparent viscosity at 60°C, for a given shear rate was decreasing, probably due to the progressing solubilisation of amylose and amylopectin and the description of starch granules. The amplitude of the

apparent viscosity changes in relation with the pasting temperature was higher for 5% maize starch paste (M5%) than for the 4% waxy (M4%) starch paste (Fig. 1). The coefficient (A) from the equation (2) was  $-10.14 (\pm 0.112)$  for the M5% against  $-4.84 (\pm 0.103)$  for the W4%. The activation energy of flow (E) from the equation (2) was respectively  $34 (\pm 1.65)$  and  $17 (\pm 2.0)$  kJ/mol for normal and waxy starch pastes (Fig. 2). The apparent viscosity of the pastes, measured at  $60^\circ\text{C}$ , was divided by a factor of 1.9 and 1.4 respectively for normal and waxy starches when the pasting temperature rose by  $10^\circ\text{C}$ . But if taking into account a quite important dispersion of the experimental results the differences in the paste viscosity can only be observed for low ( $<100^\circ\text{C}$ ) and high ( $>125^\circ\text{C}$ ) pasting temperatures.

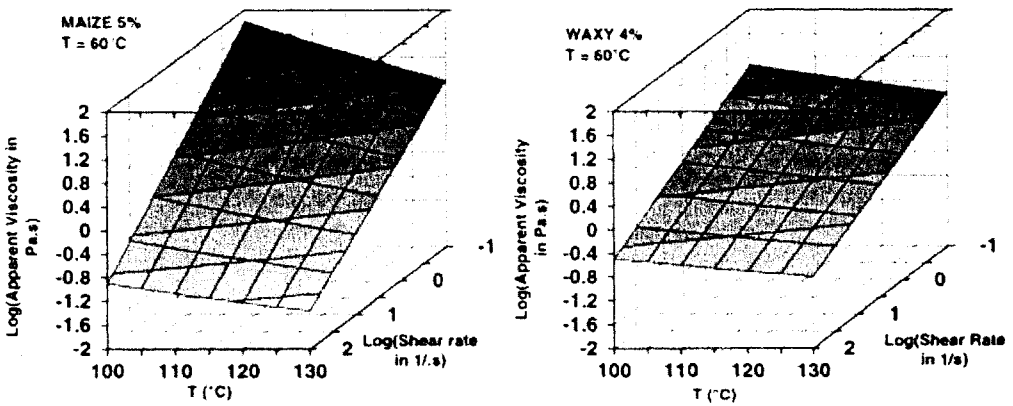


Fig. 1. Logarithm of the apparent viscosity at  $60^\circ\text{C}$  as a function of the pasting temperature and the logarithm of the shear rate for the 5% maize starch and 4% waxy starch pastes.

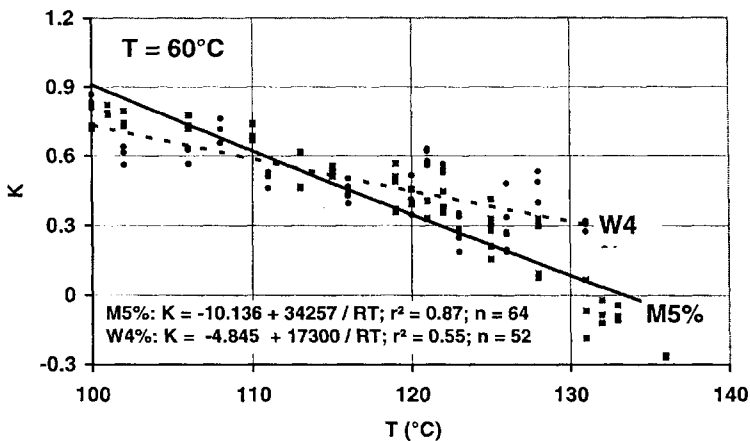


Fig. 2. Consistency index (K) at  $60^\circ\text{C}$  as a function of the pasting temperature (T in  $^\circ\text{C}$ ) for the 5% maize (M5%) starch and 4% waxy (W4%) starch pastes.

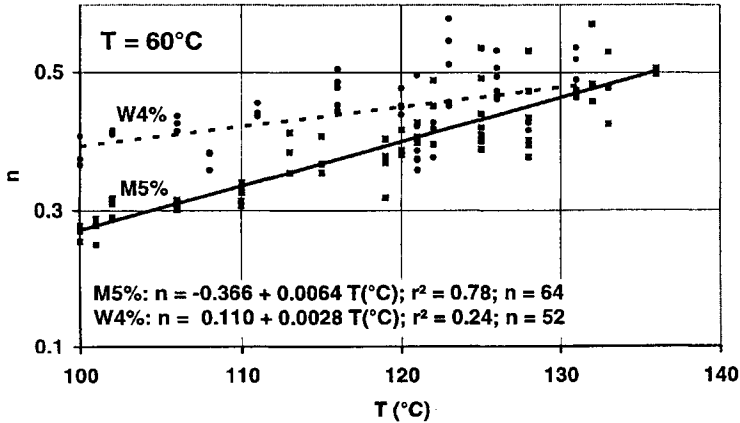


Fig. 3. Structure or behaviour index ( $n$ ) at  $60^{\circ}\text{C}$  as a function of the pasting temperature ( $T$  in  $^{\circ}\text{C}$ ) for the 5% maize (M5%) starch and 4% waxy (M4%) starch pastes.

The structure of behaviour index ( $n$ ) from the equation (1) was on average about 0.4 and it was slightly rising with the increase of the pasting temperature (Fig. 3). For both types of starch this increase was relatively small if compared with the scattering of the experimental results. The standard deviation was about 0.04, while the average amplitude of the increase of the coefficient ( $n$ ) was 0.19 for the normal and 0.09 for the waxy starch pastes for the pasting temperature rise from  $100^{\circ}\text{C}$  to  $130^{\circ}\text{C}$ .

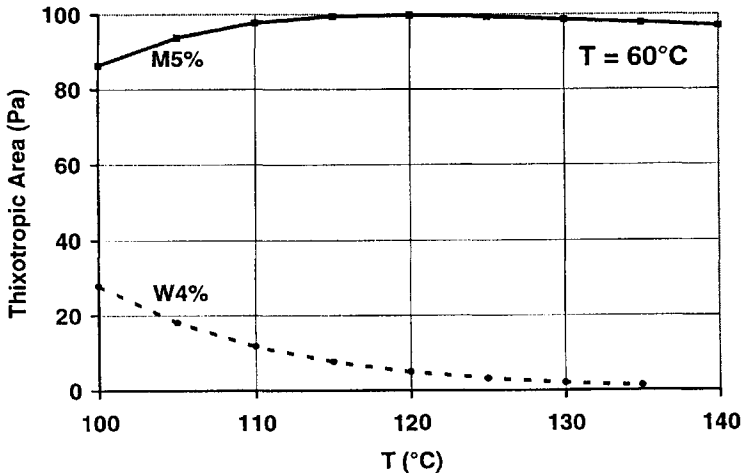


Fig. 4. Thixotropic area at  $60^{\circ}\text{C}$  as a function of the pasting temperature ( $T$  in  $^{\circ}\text{C}$ ) for the 5% maize (M5%) starch and 4% waxy (W4%) starch pastes.

Basing on the experimentally found evolution of ( $K$ ) and ( $n$ ) coefficients from the equation (1) as a function of the gelatinization temperature, we calculated the thixo-

tropic areas enclosed within the hysteresis loops for the plots of the apparent viscosity against the shear rate (Fig. 4). For the normal maize starch pastes, for the first shearing cycle, the thixotropic area at 60°C is almost independent on the gelatinization temperature. For the first cycle the thixotropic area represents 50–80% of the total area of the apparent viscosity versus shear rate plots for the increasing shear rate. It decreases to only about 20–30% for the successive shearing cycles. It means that already at 60°C the maize starch paste is quite well structured. For the waxy starch pastes the thixotropic areas decreases with the rising of the gelatinization temperature (Fig. 4). At the same time the relative importance of the thixotropic area is much smaller. It represents only between 10 and 25% of the apparent viscosity versus shear rate plots area for the increasing shear rate. This confirms the low structuring capacity of the waxy starch, composed in 99% of the amylopectin.

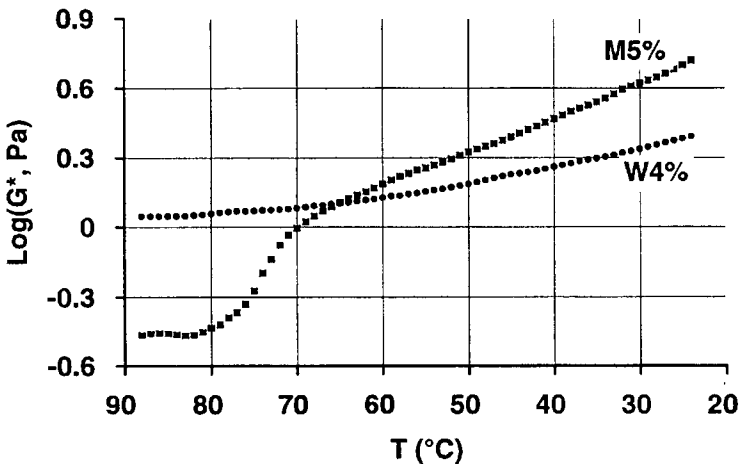


Fig. 5. Logarithm of the complex modulus ( $G^*$ ) evolution during cooling the maize 5% (M5%) and waxy 4% (W4%) pastes from 90°C to 25°C.

During the cooling from 90 to 25°C, the semi-liquid starch pastes are transformed in semi-solid gels. The complex modulus ( $G^*$ ) was gradually increasing for both types of starch, but the amplitude of the modulus rise was much higher for the M5% than for the W4% paste (Fig. 5). Also the kinetic of the modulus changes was different for both types of pastes. Between 80 and 70°C the modulus increase was very high for the M5% paste, while for the W4% paste the rate of modulus increase was low and almost uniform for the whole temperature range (90–25°C).

The shift angle was very high (~80°) for the W4% paste at 90°C and it decreased only slightly, to ~50° at 25°C (Fig. 6). For the M5% paste already at 90°C the shift angle was ~55° and it decreased rapidly between 80 and 70°C to ~35° and then

slowly to  $\sim 10^\circ\text{C}$  at  $25^\circ\text{C}$ . The shift angle is  $90^\circ$  for purely viscous bodies and  $0^\circ$  for purely elastic bodies. It is in between  $90$  and  $0^\circ$  for viscoelastic materials. From this point view the W4% paste is more viscous than elastic and the M5% paste is more elastic than viscous. This is due to the presence of amylose in the M5% pastes. Similar type of the viscosity, modulus and the shift angle evolution during cooling the potato and barley, wheat and maize starch pastes [1, 33].

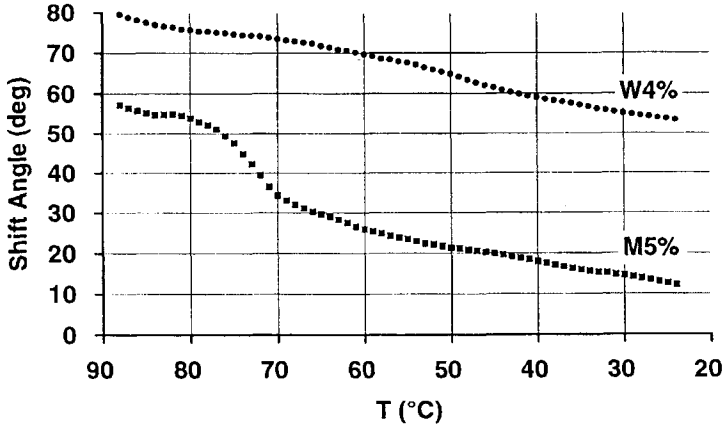


Fig. 6. Shift angle evolution during cooling the maize 5% (M5%) and waxy 4% (W4%) pastes from  $90^\circ\text{C}$  to  $25^\circ\text{C}$ .

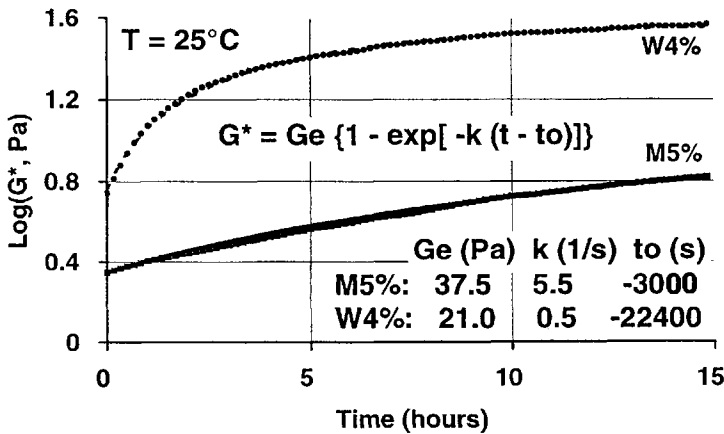


Fig. 7. Logarithm of the complex modulus ( $G^*$ ) evolution during 15 hours storage at  $25^\circ\text{C}$  of the maize 5% (M5%) and waxy 4% (W4%) pastes.

During the storage at  $25^\circ\text{C}$ , the modulus continued to grow (Fig. 7), following the kinetic of the order reaction:

$$G_t = G_e \{ 1 - \exp[-k(t - t_0)] \} \tag{3}$$

where:  $G_t$  = complex modulus level (Pa) after time  $t$  (s),  $G_e$  = equilibrium level of the complex modulus,  $t_0$  = latency time (s) and  $k$  = reaction rate constant ( $s^{-1}$ ).

All three parameters of the equation (3) were very much different for both analysed types (M5% and W4%) of starch pastes (Fig. 7). The equilibrium modulus ( $G_e$ ) was about twice higher and the reaction rate constant ( $k$ ) was  $\sim 10$  times higher for the M5% than for the W4% gels. As the gelation process was already well advanced when the product temperature was decreased to  $25^\circ\text{C}$ , so the latency time ( $t_0$ ) here is the hypothetical time period between the beginning of the storage period at  $25^\circ\text{C}$  and the moment when the modulus versus time curve, calculated by the equation (3), crosses  $G^* = 0$  Pa level.

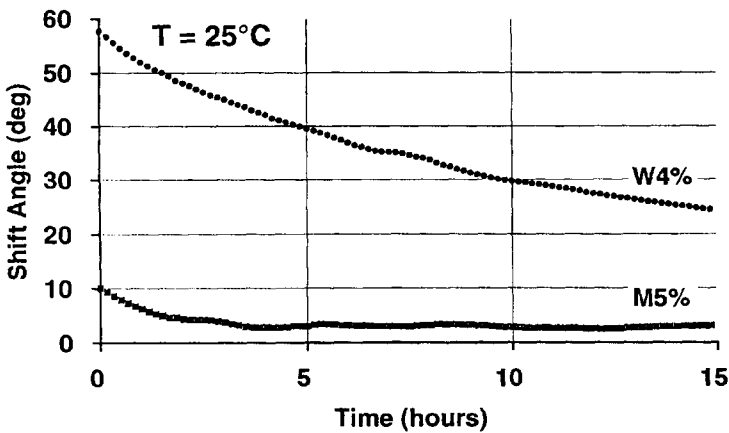


Fig. 8. Shift angle evolution during 15 hours storage at  $25^\circ\text{C}$  of the maize 5% (M5%) and waxy 4% (W4%) pastes.

The shift angle continued to decrease during the storage at  $25^\circ\text{C}$  (Fig. 8). The equilibrium level of about  $2-3^\circ$  was reached after about 3 hours of storage for the M5% gel. With the shift angle close to  $0^\circ$ , the M5% gel is almost purely elastic. On the other hand the evolution of the shift angle for the W4% gel was much slower. It passed through  $45^\circ$  level, considered sometimes as the gel point, after about 3 hours of storage at  $25^\circ\text{C}$  and it continued to decrease, reaching  $24^\circ$  after 15 hours of storage.

The starch gels, prepared from 10% normal and waxy starch suspensions have quite different microstructure (Fig. 9). In the native maize starch gel (M10%) the swollen starch granules are still visible. They have a filamentous structure and they are interconnected by a network of filaments  $0.1-0.2\ \mu\text{m}$  thick and several  $\mu\text{m}$  long. Similar filamentous structure was observed outside the starch granules in the wheat starch gels [29]. In the waxy starch gels the starch granules are observed. The gel is composed

of the small (0.1–0.2  $\mu\text{m}$ ) roughly spherical particles quite densely aggregated in grapes of variable dimensions, interconnected by the filaments, composed of more or less linearly aggregated small particles.

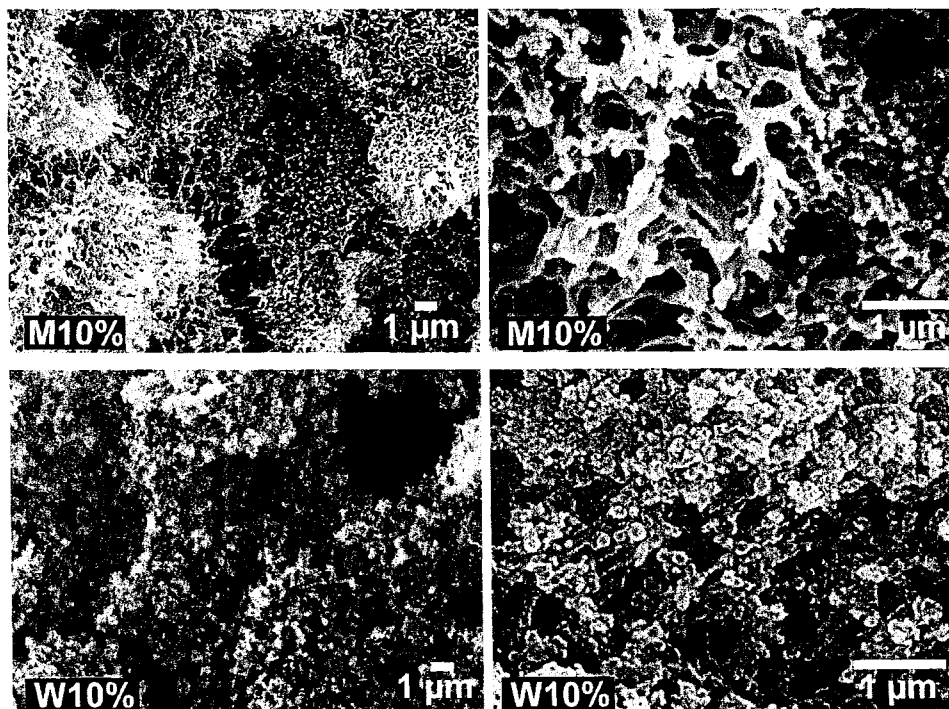


Fig. 9. Scanning electron micrographs of 10% waxy (W10%) and normal maize (M10%) starch gels.

## REFERENCES

- [1] Autio K.: Rheological and microstructural changes of oat and barley starches during heating and cooling. *Food Struct.* **9**, 1990, 297-304.
- [2] Autio K., Poutanen K., Suortti T., Pessa E.: Heat-induced structural changes in acid -modified barley starch dispersions. *Food Struct.*, **11**, 1992, 315-322.
- [3] Bagley E.B., Christianson D.D.: Swelling capacity of starch and its relationship to suspension viscosity – Effect of cooking time, temperature and concentration. *J. Text. Stud.*, **13**, 1982, 115-126.
- [4] Bagley E.B., Christianson D.D.: Yield stresses in cooked wheat starch dispersions. *Starch*, **35**, 1983, 81-86.
- [5] Bloksma A.M.: Effect of heating rate on viscosity of wheat flour doughs. *J.Text. Stud.*, **10**, 1980, 261-269.
- [6] Breton V., Korolczuk J., Doublier J.L., Maingonnat J.F.: Rheological properties of maize starch pastes and gels. *Rheology* **5**, 1995, 24-28.
- [7] Burt D.J., Russell P.L.: Gelatinization of low water content wheat starch – water mixtures. *Starch*, **35**, 1983, 354-360.



- [8] Cheng-Yi Lii, Min-Feng Lai, Mei-Lin Tsai: Studies on starch gelatinization and retrogradation with dynamic rheometry. The influence of starch granular structure and composition. *Żywność Technologia Jakość*. Proceeding of VII International Starch Convention, Kraków, 12-14 June 1996, 27-53.
- [9] Christianson D.D., Baker F.L., Loffredo A.R., Bagley E.B.: Correlation of microscopic structure of corn starch with rheological properties of cooked pastes. *Food Microstruc.*, **1**, 1982, 13-24.
- [10] Christianson D.D., Baglwey e.B.: Yield stresses in dispersion of swollen, deformable cornstarch granules. *Cereal Chem.*, **61**, 1984, 500-503.
- [11] Doublier J.L.: Rheological studies on starch – Flow behaviour of wheat starch pastes *Starch*, **33** 1981, 415-420.
- [12] Doublier J.L.: A rheological comparison of wheat, maize, faba bean and smooth pea starches. *J. Cereal Sci.*, **5**, 1987, 247-262.
- [13] Doublier J.L., Choplin L.: A rheological description of amylose gelation. *Carbohydr. Res.*, **193**, 1989, 215-226.
- [14] Doublier J.L., Llamas G., Le Meur M.: A Rheological investigation of cereal starch pastes and gels. Effect of pasting procedures. *Carbohydr. Polym.*, **7**, **1987**, 257-275.
- [15] Doublier J.L., Paton D., Llamas G.: A rheological investigation of oat starch pastes *Cereal Chem.*, **64**, 1987, 21-26.
- [16] Eliasson A.C. Viscoelastic behavior during the gelatinization of starch. I. Comparison of wheat, maaize, potato and waxy-barley starches. *J. Text. Stud.*, **17**, 1986, 253-265.
- [17] Eliasson A.C., Finstad H., Ljunger G. – 1988 – A study of starch-lipid interactions for some naative and modified maize starches. *Starch*, **40**, 1988, 95-100.
- [18] Evans I.D., Haisman D.R.: Rheology of gelatinization starch suspension. *J. Text. Stud.* **10**, 1979, 347-370.
- [19] Fujita S., Morita T., Fujiyama G.: The study of melting temperature and entalpy of starch from rice, barley, wheat, foxtail and proso millets. *Starch*, **45**, 1993, 436-441.
- [20] Gallant D.J., Guilbot A.: Etude de l'ultrastructure du grain d'amidon `a l` aide de nouvelles methodes de preparation en microscope electronique. *Staarch*, **21**, 1969, 156-163.
- [21] Gallant D.J., Guilbot A.: Developpement des connaissances sur l` ultrastructure du grain d` amidon. I. L` amidon de ble. *Starch*, **25**, 1973, 335-342.
- [22] Ghiasi K., Hosney R.C., Varriano-Marston E.: Gelatinization of wheat-starch. I. Excess-water systems. *Cereal Chem.*, **59**, 1982, 81-85.
- [23] Guilbot A., Charbonniere R., Drapon R.: Sur la contribution de l` eau a l` organisation des chaines macromoleculaires de l` amidon. *Die Starke*, **13**, 1961, 204-207.
- [24] Jane J.L., Chen J.F.: Effect of amylose molecular size and amylopectin branch chain lenght on paste properties of starch. *Cereal Chem.*, **69**, 1992, 60-65.
- [25] Korolczuk J., Breton-Dollet J.P., Tissier J.F., Maingonnat J.F.: Rheological properties and microstructure of maize starch / milk proteins gelss. *Żywność Technologia Jakość*. Processing of VII International Starch Convention, Kraków, 12-14 June 1966, 67-74.
- [26] Leach W., McCoven L.D., Schoch T.J.: Structure of the starch granule. I. Swelling and solubilitie patterns of various starches. *Cereal Chem.*, **36**, 1959, 534-544.
- [27] Miles M.J., Morris V.J., Ring S.G.: Gelation of amylose. *Carbohydr. Res.* **135**, 1985, 257- 269.
- [28] Miles M.J., Morris V.J., Orford P.D., Ring S.G.: The roles of amylose and amylopectin in the gelation and retrogradation of starch. *Carbohydr. Res.*, **135**, 1985, 271-281.
- [29] Miller B.S., Derby R.I., Trimbo H.B.: -1973- A pictorial explanation for the increase in viscosity of a heated wheat starch – water suspension. *Cereal Chem.*, **50**, 1973, 271-280.
- [30] Muhrbeck P., Eliasson A.C.: Influence of pH and ionic strength on the viscoelastic properties of starch gels – A comparison of potato and cassava starches. *Carbohydr. Polym.*, **7**, 1987 291-300.

- [31] Robin J.P., Mercier C., Charbonniere R., Guilbot A.: Lintnerized starches. Gel filtration and enzymatic studies of insoluble residues from prolonged acid treatment of potato starch. *Cereal Chem.*, **51**, 1974, 389-406.
- [32] Sterling C.: Review paper. Textural qualities and molecular structure of starch products. *J. Text. Stud.*, **9**, 1974, 225-255.
- [33] Svegmarm K., Hermansson A.M.: Shear induced changes in the viscoelastic behaviour of heat treated potato starch dispersion. *Carbohydrate Polymers*, **13**, 1990, 29-45.
- [34] Svegmarm K., Hermansson A.M.: Distribution of amylose and amylopectin in potato starch pastes: Effects of heating and shearing. *Food Structure*, **10**, 1991, 117-129.
- [35] Varriano-Marston E., Zelaznak K., Nowotna A.: Structural characteristics of gelatinized starch. *Starch*, **37**, 1985, 326-329.
- [36] Wong R.B.K., Lelievre J.: Viscoelastic behaviour of wheat starch pastes. *Rheol. Acta*, **20**, 1981, 299-307.
- [37] Wong R.B.K., Lelievre J.: Rheological characteristics of wheat starch pastes measured under steady shear conditions. *J. Appl. Polym. Sci.*, **27**, 1982, 1433-1440.
- [38] Wong R.B.K., Lelievre J.: Effects of storage on dynamic rheological properties of wheat starch pastes. *Starch*, **34**, 1982, 231-233.
- [39] Żelaznak K.J., Hosney R.C.: The glass transition in starch. *Cereal Chem.*, **64**, 1987, 121-124.
- [40] Zobel H.F.: Molecules to granules: a comprehensive starch review. *Starch*, **40**, 1988, 44-50.
- [41] Zobel H.F., Young S.N., Rocca L.A.: Starch gelatinization: an X-ray diffraction study. *Cereal Chem.*, **65**, 1988, 443-446.

## WPLYW OGRZEWANIA NA REOLOGIE I MIKROSTRUKTURĘ ŻELI ZE SKROBI KUKURYDZIANEJ

### Streszczenie

W temperaturze 60°C lepkość kleików, z normalnej i woskowej skrobi kukurydzianej, obniżyła się wraz ze wzrostem prędkości ścinania. Dla zakresu temperatury kleikowania od 100 do 130°C, indeks konsystencji był odwrotnie proporcjonalny do temperatury kleikowania. Indeks struktury był średnio na poziomie 0,4 i bardzo nieznacznie wzrastał z temperaturą kleikowania. Kleiki z normalnej skrobi kukurydzianej wykazywały znacznie wyższe własności tiksotropowe niż ze skrobi woskowej. Proces żelowania w temperaturze 25°C przebiegał zgodnie z kinetyką reakcji pierwszego rzędu. Stała prędkości reakcji była około 10 razy niższa dla skrobi woskowej. Żele ze skrobi normalnej miały strukturę włóknistą, natomiast ze skrobi woskowej charakteryzowały się strukturą ziarnistą. ☒