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Influence of starch sodium octenyl succinate on rheological behaviour of wheat flour dough systems

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Abstract

Experimental and theoretical influence of addition of various amounts of three types starch sodium octenyl succinate (OSA) granules (0-20%): a) non-physically modified, b) pregelatinized and c) hydrolyzed spray-dried on rheological behaviour of wheat flour dough systems under oscillatory strain conditions was considered. Mathematical model was developed based on the internal variable theory by introducing the fractional derivatives to describe anomalous nature of energy dissipation. Two model parameters were used for quantitative description of the rheological behaviour of the systems: the effective modulus and the dumping coefficient.

The most rigid system with pronounced dumping effects was the dough supplemented with 20% of the non-physically modified OSA starch granules (maximum of the effective modulus and minimum of the dumping coefficient), while the softest system was the dough with 20% of the pregelatinized OSA starch. The obtained results revealed that the rheological behaviour of OSA starch supplemented dough depended on the OSA starch granule rigidity, i.e. extent of OSA starch granule disintegration and polysaccharide degradation.

Keywords: Rheology, Mathematical modeling, Microstructure, Starch sodium octenyl succinate (OSA starch), Wheat flour dough
1. Introduction

Application of hydrocolloids as bread improvers has been extensively investigated in recent years (Guarda et al., 2004; Kohajdová et al., 2009). Although natural hydrocolloids have unique functional properties, they are also characterized with certain limitations such as water insolubility, instability at low pH, etc. which restrict their overall utilization (Milani & Maleki, 2012). These limitations can be overcome by different chemical modification of the natural hydrocolloids. In addition, chemical modifications of hydrocolloids ensure their uniform properties, in contrast to the hydrocolloids from natural sources where a high variation in properties can be found due to processing and origin (Guarda et al., 2004).

Polymers with a wide range of functional properties can be created in a reaction where hydroxyl groups are substituted with different side chains such as methyl, hydroxypropyl, carboxymethyl groups. Addition of hydrophobic groups to hydrophilic polymer, or vice versa, leads to a polymer with a high surface activity. One of the well known emulsifying hydrocolloid is hydroxypropyl methylcellulose (HPMC) which is used in breadmaking due to its ability to retard the staling and improve the quality of the fresh products.

Beside cellulose, starch can also be chemically modified to become amphiphilic and thus can act as an effective emulsifier. Such emulsifying starch is octenyl succinate starch (OSA starch). There are a lot of advantages of using starch as raw material for modification. Beside cellulose it is most abundant naturally occurring polysaccharide available from plant kingdom. Moreover, it is characterized with low-cost, biocompatibility, biodegradability, non-toxicity, etc.
In contrast to emulsifying cellulose derivatives (Guarda et al., 2004; Lazaridou et al., 2007), there is very little information concerning the role of emulsifying starch in breadmaking. Taking into account the fact that other starch substitutes have exhibited significant bread improving properties in terms of crumb texture (Miyazaki et al., 2006) and that OSA starch has special nutritional values since it can act as functional fibre (Heacock et al., 2004) it is of a great importance to investigate the feasibility of OSA starch as bread improver.

For improving the quality of baked products it is essential to consider rheological behaviour of wheat flour dough systems with various types of OSA starch granules. However, finding a constitutive model that has all accurate molecular and structural arguments to simulate the linear and non-linear properties of the systems is a tough challenge due to the complex nature of the systems. All constituents: gluten proteins, polar and non polar lipids, water, native starch granules and various types OSA starch granules integrally contribute to rheological behaviour of the systems dependently on density of covalent and non covalent bonds and rigidity of the system constituents.

Bread dough is a viscoelastic and shear thinning material combined of Hookean solid and non-Newtonian viscous liquid (Mirsaeedghazi et al., 2008). Various mechanical analogue models have been developed based on series and parallel combination of springs, dashpots and shear pins (Tanner et al., 2008). Some of them are difficult for analytical solving and light only parts of the complex phenomenon of dough rearrangement under various loading conditions. For deeper insight of the rheological response of the dough systems it is necessary to consider various types of interactions between the constituents on various spatial scales. Such interactions induce dumping effects in rheological
responses of the dough systems. Dumping effects should be connected with anomalous nature of energy dissipation and mathematically formulated by applying fractional derivatives (Podlubny, 1999; Metzler & Klafter, 2000).

The aim of this consideration was to formulate the constitutive model equation by applying the internal variable theory (Coleman & Gurtin, 1967; Trumel et al., 2001; Atanackovic, 2002) for estimating non reversible nature of the phenomenon. The theoretical approach was modified by introducing the fractional derivatives to describe the anomalous nature of energy dissipation.

The developed model equation was used to describe rheological behaviour of the dough systems with various amounts of three types of OSA starch granules (0-20 w%): a) non-physically modified, b) pregelatinized and c) hydrolyzed spray-dried. The aim was to establish the role of the OSA starch as bread improver and analyze the possible interactions with the dough constituents. Microstructure of the dough in the presence of OSA starches and its relationship with the dough behaviour under oscillatory strain conditions was also monitored.

2. Materials and methods

2.1. Materials

Wheat flour (12.9% moisture content, 11.9% protein, 0.64% ash) was obtained from the Fidelinka milling company AD, Serbia. Modified starches used in this study, provided by Cargill, France, included: non-physically modified starch sodium octenyl succinate
(C*EmTex 06328), pregelatinized starch sodium octenyl succinate (C*EmTex 12688) and hydrolyzed, spray-dried starch sodium octenyl succinate (C*EmCap 12633). All three starches were modified waxy maize starches.

2.2. Rheological measurements

Rheological behaviour of OSA starch solutions and wheat flour doughs containing OSA starches in a concentration of 0, 5, 10, 15 and 20% was monitored with a HAAKE Mars rheometer (Thermo Scientific, Germany) at 30 °C. Flow curves were monitored only for a) pregelatinized and b) hydrolyzed spray-dried OSA starches, since non-physically modified OSA starch was insoluble in cold water, and thus formed a suspension which particles settled down to the bottom of the cylinder, leading to sample inhomogeneity and measurement non-repeatability.

Flow curves of two types of 5% OSA starch solutions in cold water (30 °C) were recorded by performing hysteresis loop tests. Shear rate was continually increased from 0 to 200 s⁻¹, remained constant at 200 s⁻¹ and decreased to 0 s⁻¹, while the duration of each step was 120 s. The measuring geometry used was double gap cylinder system DG41 for low viscous solutions and coaxial cylinder Z20 for higher viscosity samples.

Dough was rheologically characterized with small deformation dynamic oscillatory tests. The measurements were performed using parallel plate geometry (PP35S, 35 mm diameter) which was serrated in order to avoid slippage. The doughs for rheological experiments were prepared using a Mixolab (Chopin Technologies, France) mixing bowl. The samples were kneaded at Mixolab water absorption (which was previously
determined as a percentage of water required for the dough to produce a torque of 1.1±0.05 Nm, on 14% moisture basis. The following settings were used: mixing speed 80 rpm, dough weight 75 g, tank temperature 30°C, mixing time was determined as a time required for dough to reach the consistency of 1.1 Nm (ranged from 2.5 to 5.5 min, depending on a sample). The dough was rested for 10 min in a closed plastic bag at 30°C. Subsequently, a sample was taken from the inner part of the dough, loaded between the plates and the gap adjusted to 1 mm. The excess material was removed with a spatula and the exposed sample edge was covered with a thin layer of light paraffin oil to prevent evaporation during measurements. The sample was rested between the plates for 10 min before testing to allow residual stresses to relax. Mechanical spectra (frequency sweeps) were recorded over the range 1–10 Hz at 2 Pa stress (which was within the linear viscoelastic region).

2.3. Scanning Electron Microscopy (SEM)

OSA starches as well as dough samples in which wheat flour was partially replaced with OSA starches were observed in a Jeol JSM 6460LV scanning electron microscope (Tokyo, Japan) with a 25-kV acceleration voltage. While OSA starches were just coated with gold, dough samples before being gold sputtered were previously prepared. The preparation involved placing the dough pieces in 3% glutaraldehyde for two hours and dehydratation in a graded acetone series (25, 50, 75, 80 and 100%) for 20 min followed by drying with a CPD 030 BAL-TEC Critical Point Dryer (BAL-TEC AG, Liechtenstein).
2.4. Statistical analysis

All samples were prepared and analyzed in triplicates and the results were reported as mean ± standard deviation. Analysis of variance (ANOVA) followed by Tukey test with 0.05 significance level were used to assess significant differences among the means. ANOVA was carried out with the Statistica 10 (StatSoft Inc., USA).

3. Model development

Dough is complex system made by partially connected protein network with embedded starch granules. Polar lipids are incorporated in the network while non-polar lipids form vesicles embedded within the network. Both of them significantly contribute to the rheological response of the dough systems. Addition of various amount of starch sodium octenyl succinate (OSA) to improve nutritional quality of the bread as well as bread crumb structure and texture significantly influences the rheological behaviour of the systems. Various kinds of interactions between the constituents of the systems cause the specific effects of energy dissipation and induce non-linear rheological behaviour (Glucklich & Shelef, 1962; Mirsaedghazi et al., 2008). The systems rearrangement under various loading conditions includes conformational changes of polymer chains, partial disruption of some non covalent bonds and orientation of starch granules in the field. The structural changes of the systems induce generation of: (1) repulsive forces between the same charged segments of the system constituents and (2) attractive forces
between the opposite charged segments which tend to keep the structural integrity and
cause the damping of energy dissipation. The damping effects should be connected with
the non-linear nature of the systems rheological responses.

Deeper insight into the non-linear rheological responses is necessary for improving the
rheological and nutritional performances of the examined systems. Consequently, we
model the intrinsic dynamics of the dough structural rearrangement by applying the
internal variable theory in one side and introducing the fractional derivatives in the other.

The internal variable theory has been used for describing the impact of energy dissipation
on various system rheological responses (Coleman and Gurtin, 1967; Trumel et al., 2001;
Atanackovic, 2002). On that base, the state of the systems is described by the total shear
strain component $\gamma(t)$ and the internal variable $\xi(t)$ as well as by the specific
thermodynamics variables. The specific thermodynamic variables as: $u(t)$ the internal
energy, $s(t)$ the entropy and the Helmholtz free energy $u(t) - T s(t)$ depends on the total
shear strain component $\gamma(t)$ and the internal variable $\xi(t)$. The internal variable
represents the irreversible part of the total shear strain.

The main task in the lighting of the dissipative phenomena is the postulating of the
relationship between the total shear strain component $\gamma(t)$ and its irreversible part $\xi(t)$
and further verification of the assumption by comparing model prediction with
experimental data. We assume that changes of the total shear strain component
simultaneously induce changes of its irreversible part in the form: $\_\_0 D^\alpha_t(\gamma(t)) = \_\_0 D^\alpha_t(\xi(t))$
(where $\_\_0 D^\alpha_t(\bullet) = \frac{d^\alpha}{dt^\alpha}(\bullet)$ is the fractional derivative of some function). Reversible part of
the total shear strain component increases more rapidly up to its maximum value and stay
approximately constant during experimental time period. For this condition, the changes
of the specific Helmholtz free energy under isothermal conditions could be expressed as:

$$\rho \int_0^t (u(t) - T \cdot s(t)) = (\sigma_r(t) - \Theta(t)) \int_0^t (\gamma(t))$$

(1)

where $\rho$ is the system averaged density, $\sigma_r(t)$ is the component of total shear stress,
$\Theta(t)$ is the component of the irreversible part of the stress, $\int_0^t (f(t)) = \frac{d^\alpha}{dt^\alpha} (f(t))$ is the
fractional derivative of some function $f(t)$ while $\alpha$ is the order of the fractional
derivatives (the dumping coefficient). Caputo’s definition of the fractional derivative of a
function $f(t)$, was used and it is given as follows (Poklubny, 1999):

$$\int_0^t \frac{d^\alpha}{dt^\alpha} (f(t)) = \frac{1}{\Gamma(1-\alpha)} \frac{d}{dt} \int_0^t \frac{f(r)}{(r-t)^\alpha} dr$$

(2)

where $t$ is an independent variable (time) and $\Gamma(1-\alpha)$ is the gamma function. If
parameter $\alpha$ is $\alpha = 0$, we obtain $\int_0^t (f(t)) = f(t)$. When $\alpha = 1$, the corresponding gamma
function $\Gamma(1-\alpha) \rightarrow \infty$. For this case, the fractional derivative is not defined. However, it
can be shown, that in the limit when $\alpha \rightarrow 1$, follows $\int_0^t (f(t)) \rightarrow \dot{f}(t)$, where the dot
denotes the first time derivative. Thus, when $0 \leq \alpha < 1$, the equation 1 describes the
dumped dissipative phenomena. Smaller value of the parameter $\alpha$ points to more
pronounced dumping effects.

It was assumed that the component of total shear stress $\sigma_r(t)$ and the component of the
irreversible part of stress $\Theta(t)$ represent the linear functions of the variables $\gamma(t)$ and
$\xi(t)$. Non-linear nature of the systems rheology is connected with the dumping effects.
The component of total shear stress $\sigma_r(t)$ and the component of the irreversible part of stress $\Theta(t)$ are expressed as:

$$\sigma_r(t) = \kappa_1 \gamma(t) + \kappa_2 \xi(t) \quad \text{and}$$

$$\Theta(t) = \beta_1 \gamma(t) + \beta_2 \xi(t)$$

where $\kappa_1$ and $\beta_1$ are the moduli which quantify the reversible part while $\kappa_2$ and $\beta_2$ are the moduli which quantify the irreversible part of the phenomenon. The stress difference expressed as $\sigma_r(t) - \Theta(t)$ represents the component of the reversible (elastic) part of the stress.

In further consideration, changes of the specific internal energy and changes of the specific entropy were expressed and returned to eq. 1. The specific internal energy is expressed based on the first law of thermodynamics by including the dumping effects as:

$$\rho_0 D^\sigma_r(u(t)) = \rho D^\sigma_r(Q(t)) + \sigma_r(t)_{0} D^\sigma_r(\gamma(t))$$

where $Q(t)$ is the specific heat production during the systems rearrangement. The second term on the right hand side represents changes of the mechanical work. The specific entropy is expressed based on the second law of thermodynamics for closed systems as:

$$\rho_0 D^\sigma_s(s(t)) = \frac{1}{T} D^\sigma_s(Q(t)) + \rho_0 D^\sigma_s(s(t))$$

where $\rho_0 D^\sigma_s(s(t))$ represents the total production of entropy while $\rho_0 D^\sigma_s(s(t))$ represents the internal production of entropy which satisfy condition $\rho_0 D^\sigma_s(s(t)) \geq 0$ for irreversible processes. The internal production of entropy during rearrangement of dough systems is determined after introducing eqs. 4 and 5 into eq. 1. It is expressed as:

$$\rho_0 D^\sigma_r(s(t)) = \frac{\Theta(t)}{T} D^\sigma_r(\gamma(t)) \geq 0$$
We have indicated that the entropy production is positive. The inequality \( 6 \) may be satisfied by setting:

\[
\Theta(t) = \psi \, D_t^\alpha (\gamma(t))
\]  
(7)

where \( \psi \) is the modulus which quantified the irreversible phenomenon caused by changes the component of the total shear strain.

Constitutive equation for the rearrangement of dough systems under oscillatory strain conditions is formulated from eqs. 3 and 7 by eliminating the internal variable \( \xi(t) \) and the irreversible component of stress \( \Theta(t) \). It is expressed as:

\[
\sigma_t(t) = G_s \, \gamma(t) + \eta \, D_t^\alpha (\gamma(t))
\]  
(8)

where \( G_s \) is the static modulus of elasticity equal to \( G_s = \kappa_1 - \kappa_2 \frac{\beta_1}{\beta_2} \) and \( \eta \) is the effective modulus equal to \( \eta = \psi \, \frac{\kappa_2}{\beta_2} \). The static modulus combines the reversible and irreversible parts of the phenomenon. However, the effective modulus represents the measure of local irreversible processes of the systems structural organization. The first term of the right hand side of eq. 8 represents the reversible (elastic) part and the second term represents the irreversible (viscous) part of the component of total stress. If the parameter \( \alpha \) is \( \alpha = 0 \), we obtain \( D_t^0 (\gamma(t)) = \gamma(t) \). For such case the second term of eq. 8 additionally contributes to elastic Hookean behaviour. When \( \alpha \to 1 \), we obtain \( D_t^\alpha (\gamma(t)) \to \dot{\gamma}(t) \). For such case, the second term represents the purely viscous contribution to the total stress.

Development constitutive model equation proposed for describe the rearrangement of the dough systems is the modified to Kelvin-Voigt type model with fractional derivatives.
Various fractional forms of Kelvin-Voigt model have been used for describing non-linear responses of viscoelastic solid systems (Djordjevic et al, 2003). However, little has been reported about the corresponding intrinsic dynamics of the systems rearrangement which represents the course of the non-linear response.

Eq. 8 was transformed from the time domain into the frequency domain using the Fourier integral transform. Transforming equation is expressed in the form

\[ F[\sigma(t)] = G^* F[\chi(t)] \]

where \( F \) is the Fourier operator and \( G^* \) is the complex dynamic modulus equal to \( G^* = G' + iG'' \), while \( G' \) is the storage modulus and \( G'' \) is the loss modulus and \( i = \sqrt{-1} \) is the imaginary unit. Fourier transform of the fractional derivative of the component of shear strain \( \chi(t) \) is expressed as

\[ F[D^\alpha \chi(t)] = (i\omega)^\alpha F[\chi(t)] \]

where \( \omega \) is the angular frequency (Djordjevic et al, 2003).

The storage and loss moduli are expressed as:

\[ G'(\omega) = G_s + \eta \omega^\alpha \cos \left( \frac{\pi \alpha}{2} \right) \]

\[ G''(\omega) = \eta \omega^\alpha \sin \left( \frac{\pi \alpha}{2} \right) \]

(9)

where the storage modulus \( G'(\omega) \) quantify the elastic behaviour and the loss modulus \( G''(\omega) \) quantify the viscous behaviour of the dough systems.

Model parameters: \( G_s \) the static modulus of elasticity, \( \eta \) the effective modulus and \( \alpha \) the dumping coefficient (the order of fractional derivatives) should be determined by comparing experimental data sets \( G'(\omega) \) vs. \( \omega \) and \( G''(\omega) \) vs. \( \omega \) for various dough systems with the model predictions.
4. Results and discussion

Rheological behaviour of the wheat flour dough systems with various amounts of three types OSA starch granules (0 - 20%): a) the non-physically modified, b) the pregelatinized and c) the hydrolyzed spray-dried was estimated based on the developed model. Since OSA modified starch granules originated from waxy maize starch, they contained less than 1% amylose (Jane, 2009), and therefore they could be considered as OSA modified amylopectin chains organized into granules. OSA starch amylopectin molecules were able to form hydrophilic and hydrophobic bonds with other constituents of the systems (native starch, proteins, water, polar and non-polar lipids). Possibility of non-covalent bonds formation depends on effective external surface of the OSA granules. The effective external surface of the OSA starch granules was the highest for the non-physically modified OSA starch granules (Figure 1 B) and the lowest for pregelatinized OSA starch granules (Figure 1 D). The pregelatinized starch which was thermally and mechanically treated using drum drier gave irregular, flat particles (Figure 1 D). On contrary, the spray-dried OSA starch was characterized by spherical particles (Figure 1 F). Higher density of non-covalent bonds should induce formation of the more rigid dough systems. For physically modified OSA granules, the effective external surface fluctuated around some averaged values in oscillatory field conditions dependently on their structural organization.

Rheological behaviour of the systems with additions of the OSA starches also depended on rigidity of OSA starch granules themselves. Rigidity could be correlated with ability
to water absorption. The ability to water absorption depended on: ordering of amylopectin chains and chain molecular weight distribution.

The most rigid was the non-physically modified OSA starch (Figure 1 B) which in a dough system acted as inert filler embedded into gluten. It is in accordance with mostly preserved crystalline structures after treatment of starch with octenyl succinic anhydride. However, small fraction of formed amorphous regions induced higher water absorption as compared to native starch (Table 1).

The softening of physically modified OSA starch granules was induced by thermal and mechanical treatments. Drum-drying and spray drying methods of modifications additionally destroyed the crystalline structures responsible for the integrity of the granules. Consequently, these techniques produced modified food starch that swell in cold water (Wurzburg, 2006). It was caused by amorphous structure of these granules.

Higher water absorption of the systems with addition of the pregelatinized OSA starches as compared to the non-physically modified OSA starch represented the consequence of amorphous, more open porous structure of the pregelatinized OSA starches (Table 1).

However, addition of the hydrolyzed spray-dried OSA starch induced decrease of dough water absorption as compared to the control system. Enzymatic hydrolysis of amylopectin chains caused decrease in amylopectin molecular weight and thus lower ability to water absorption of these granules.

In order to estimate the morphological characteristics of physically modified OSA starches, flow curves of 5% cold water solutions of: the pregelatinized OSA starches and the hydrolyzed spray-dried OSA starch were monitored (Figure 2). The viscosity of the 5% hydrolyzed spray-dried OSA starch water solution was much lower than the viscosity
of the 5% pregelatinized OSA starch water solution. It was in accordance with the facts that averaged molecular weight of amylopectin molecules was much lower in the case of the hydrolyzed spray-dried OSA starches. Rheological behaviour of the systems with the addition of various OSA starch granules was considered under oscillatory strain conditions. The predicted values of the moduli were calculated using constitutive eq. 9.

As shown in Figure 3 A-B, the model prediction values for the dough systems with various amounts of the non-physically modified OSA starch granules (Figure 1 B) correlated well with the one representative corresponding experimental set, with relative error of 10%. The optimal model parameters obtained by this fitting procedure that enable the best comparison with the experimental data where shown in Table 2. Addition of various amounts of the non-physically modified OSA starch granules induced reinforcement of the dough systems. It was in accordance with the fact that: (1) the non-physically modified OSA starch granules were the most rigid and (2) the effective external surface of the non-physically modified OSA starch granules was the highest. It pointed to maximum of non-covalent bonds density. Since OS groups are more located on the immediate surface of the modified starch granules then in the bulk (Sweedman et al., 2010), high specific surface of the granule with high number of exposed OS groups increased the reactive surface area and therefore the possibility of interaction among dough constituents. This led to stronger, more rigid dough in comparison to control sample.

As shown in Figure 4 A-B, the model prediction values for the dough systems with various amounts of the pregelatinized OSA starch (Figure 1 D) correlated well with the
one representative corresponding experimental set, with relative error of 10%. The optimal model parameters obtained by this fitting procedure that enable the best comparison with the experimental data where shown in Table 2. Addition of various amounts of the pregelatinized OSA starch granules induced softening of the dough systems. It was in accordance with the fact that: (1) the effective external surface of the pregelatinized OSA starch granules was the smallest and (2) the technological treatment of formation the pregelatinized OSA starch granules leaded to the granule crystalline structure destruction. A higher degree of macromolecular disorganization led to higher solubility of these starches which formed viscous pseudoplastic systems (Figure 2). Therefore, in dough these OSA starches increased water absorption (Table 1). Due to loss crystallinity and higher amount of water in the system pregelatinized OSA starch yielded softer, sticker and weaker dough systems in comparison to control, in which gluten structural continuity was affected (Figure 1 E).

As shown in Figure 5 A-B, the model prediction values for the dough systems with various amounts of the hydrolyzed spray-dried OSA starch granules (Figure 1 F) correlated well with the one representative corresponding experimental set, with relative error of 10%. The optimal model parameters obtained by this fitting procedure that enable the best comparison with the experimental data where shown in Table 2. Addition of various amounts of the hydrolyzed spray-dried OSA starch granules also induced softening of the dough systems. The softening in such case was not so pronounced as for the systems with additions of the pregelatinized OSA starch granules. It represented the consequence of low ability to water absorption of hydrolyzed amylopectin chains. Hydrolysis led to decrease of the molecular weight and consequently to decrease in
solution viscosity (Figure 2). Low amount of water induced formation of more rigid structure as compared to the system containing pregelatinized OSA granules. However, the hydrolyzed spray-dried OSA granules were significantly softer than the non-physically modified OSA starch granules due to: (1) amorphous structure and (2) low molecular weight of amylopectin chains. Therefore, when added to wheat flour, these starches decreased flour water absorption (Table 1) and yielded the dough of weakened structure (Figure 1 G).

Rheological behaviour of examined systems was quantified by the model parameters. The values of static modus for all systems were $G_j = 0$. It indicated to anomalous energy dissipation as the dominant mechanism of the systems rearrangement under oscillatory strain conditions. Anomalous nature of the phenomenon was connected with the dumping effects of conformational ordering of protein chains resulted by: (1) the protein chains rigidity, (2) presence of the dispersed or swollen starch granules (native and OSA), (3) the covalent and non covalent bonds between the constituents within the systems which induced their rigidity as a whole. The dumping effects should be connected with non-linear nature of the rheological responses of the examined systems.

The mean values of the model parameters and the corresponding standard deviations, shown in Table 2, were determined by comparing the model predictions with the three repeated experimental sets for every experimental condition. The dough systems notations were: a) the non-physically modified, b) the pregelatinized and c) the hydrolyzed spray-dried OSA starch granules. The notations were the same as in the Figures 3-5 (A, B).
The effective modulus $\eta$ (Table 2) increased with the increase in the amount of non-physically modified OSA starch granules (Figure 1 B). It quantified increase of the system rigidity due: rigidity of added non-physically modified OSA starch granules and increased density of non covalent bonds. At the same time, the dumping coefficient $\alpha$ decrease as the results of increase in the density of non covalent bonds. These systems showed lower ability of adaptation to oscillatory strain condition with pronounced dumping effects. However, the addition of the pregelatinized and the hydrolyzed spray-dried OSA starch granules (Figure 1 D and F) induced decrease of the effective modulus $\eta$ with increase in the amount of OSA starch. It represented the consequence of addition of OSA granules with weakened or destroyed crystalline structures responsible for the integrity of the granule. At the same time, the softening of these systems was quantified by higher values of the dumping coefficient $\alpha$. The relation between the effective modulus and the dumping coefficient could be expressed as: $\eta \sim \alpha^{-1}$.

5. Conclusions

Addition of various types of OSA starch granules (the non-physically modified, the pregelatinized and the hydrolyzed spray-dried) to the wheat dough systems significantly influenced the system rheological behaviour. It primarily depends on the rigidity of added OSA starch granules and their effective external surfaces. Higher effective surfaces induced higher density of hydrophilic and hydrophobic bonds between the system constituents. Consequently, addition of various amounts of the non-physically modified OSA starch granules induces the system reinforcement. On the other side, addition of
various amounts of the pregelatinized and the hydrolyzed spray-dried OSA starch granules induces the system softening. Rheological behaviour of the examined system is described based on the developed model by introducing the assumption that changes of the total shear strain component simultaneously induce changes of its irreversible part while the reversible part more rapidly reaches its maximum value. The results points to anomalous dissipation of energy due to the system rearrangement as the dominant mechanism of their responses to oscillatory strain conditions. Anomalous mechanism is quantified by introducing the fractional derivatives and the dumping coefficient $\alpha$ on one side and the effective modulus $\eta$ on the other.

Maximum of the effective modulus and minimum of the dumping coefficient corresponded to the dough system with 20 % of the non-physically modified OSA starch granules which acted as inert filler with high effective surfaces modified with OS groups which increased the possibility of interactions with other dough constituents. This was the most rigid system which pronounced dumping effects. On the other side, minimum of the effective modulus and maximum of the dumping coefficient corresponded to the dough system with 20 % of the pregelatinized OSA starch granules. It represented the consequence of the modification technique which destroyed the crystalline structures responsible for the integrity of the granule.

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References


Figure captions

**Fig. 1 A-G.** SEM photomicrographs of the control dough (A), non-physically modified OSA starch before (B) and after incorporation in dough (C), pregelatinized OSA starch before (D) and after incorporation in dough (E) and the hydrolyzed spray-dried OSA starch before (F) and after incorporation in dough (G)

**Fig. 2.** Flow curves of 5% water solutions of the pregelatinized and the hydrolyzed spray-dried OSA starches

**Fig. 3 A-B.** Storage (A) and loss (B) moduli as a function of frequency for the dough system with addition of the 0-20 % of the non-physically modified OSA starch (the dough system noted as a)

**Fig. 4 A-B.** Storage (A) and loss (B) moduli as a function of frequency for the dough system with addition of the 0-20 % of the pregelatinized OSA starch (the dough system noted as b)

**Fig. 5 A-B.** Storage (A) and loss (B) moduli as a function of frequency for the dough system with addition of the 0-20 % of the hydrolyzed spray-dried OSA starch (the dough system noted as c)
Table 1. Mixolab water absorption values of control dough and doughs containing OSA starches in different concentrations

<table>
<thead>
<tr>
<th>Dough systems</th>
<th>Water absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control-0% OSA starch</td>
<td>55.4±0.1 e</td>
</tr>
<tr>
<td>Non-physically modified OSA starch (a)</td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>56.0±0.1 f</td>
</tr>
<tr>
<td>10%</td>
<td>56.1±0.1 f</td>
</tr>
<tr>
<td>15%</td>
<td>56.8±0.1 g</td>
</tr>
<tr>
<td>20%</td>
<td>56.9±0.1 g</td>
</tr>
<tr>
<td>Pregelatinized OSA starch (b)</td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>59.6±0.1 i</td>
</tr>
<tr>
<td>10%</td>
<td>59.0±0.1 h</td>
</tr>
<tr>
<td>15%</td>
<td>61.0±0.1 j</td>
</tr>
<tr>
<td>20%</td>
<td>63.1±0.1 k</td>
</tr>
<tr>
<td>Hydrolyzed spray-dried OSA starch (c)</td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>53.8±0.2 d</td>
</tr>
<tr>
<td>10%</td>
<td>52.3±0.1 e</td>
</tr>
<tr>
<td>15%</td>
<td>50.0±0.1 b</td>
</tr>
<tr>
<td>20%</td>
<td>47.2±0.2 a</td>
</tr>
</tbody>
</table>

Values followed by the same letter in the column are not significantly different (p > 0.05)
**Table 2.** The model parameters

<table>
<thead>
<tr>
<th>Dough systems</th>
<th>( \alpha ) ((^{-}))</th>
<th>( \eta ) (Pa s(^{\alpha}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control-0% OSA starch</td>
<td>0.225±0.01(^{b})</td>
<td>((0.70±0.01^{g})\times10^{4})</td>
</tr>
<tr>
<td>Non-physically modified OSA starch (a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 %</td>
<td>0.190±0.01(^{a})</td>
<td>((1.00±0.01^{b})\times10^{4})</td>
</tr>
<tr>
<td>10 %</td>
<td>0.187±0.01(^{a})</td>
<td>((1.35±0.01^{a})\times10^{4})</td>
</tr>
<tr>
<td>15 %</td>
<td>0.186±0.01(^{a})</td>
<td>((1.50±0.01^{b})\times10^{4})</td>
</tr>
<tr>
<td>20 %</td>
<td>0.185±0.01(^{a})</td>
<td>((1.56±0.01^{k})\times10^{4})</td>
</tr>
<tr>
<td>Pregelatinized OSA starch (b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 %</td>
<td>0.245±0.01(^{b})</td>
<td>((0.46±0.01^{a})\times10^{4})</td>
</tr>
<tr>
<td>10 %</td>
<td>0.250±0.01(^{b})</td>
<td>((0.33±0.01^{c})\times10^{4})</td>
</tr>
<tr>
<td>15 %</td>
<td>0.320±0.01(^{d})</td>
<td>((0.13±0.01^{a})\times10^{4})</td>
</tr>
<tr>
<td>20 %</td>
<td>0.340±0.01(^{d})</td>
<td>((0.11±0.01^{a})\times10^{4})</td>
</tr>
<tr>
<td>Hydrolyzed spray-dried OSA starch (c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 %</td>
<td>0.230±0.01(^{b})</td>
<td>((0.70±0.01^{g})\times10^{4})</td>
</tr>
<tr>
<td>10 %</td>
<td>0.235±0.01(^{b})</td>
<td>((0.55±0.01^{b})\times10^{4})</td>
</tr>
<tr>
<td>15 %</td>
<td>0.240±0.01(^{b})</td>
<td>((0.39±0.01^{d})\times10^{4})</td>
</tr>
<tr>
<td>20 %</td>
<td>0.290±0.01(^{c})</td>
<td>((0.23±0.01^{b})\times10^{4})</td>
</tr>
</tbody>
</table>

Values followed by the same letter in the column are not significantly different (\( p > 0.05 \))
Fig. 1 A-G
Fig. 2

Fig. 3 A-B
Fig. 4 A-B
Fig. 5 A-B.