



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

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

3

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20 **Abstract**

21

22 Experimental and theoretical influence of addition of various amounts of three types  
23 starch sodium octenyl succinate (OSA) granules (0-20%): a) non-physically modified, b)  
24 pregelatinized and c) hydrolyzed spray-dried on rheological behaviour of wheat flour  
25 dough systems under oscillatory strain conditions was considered.

26 Mathematical model was developed based on the internal variable theory by introducing  
27 the fractional derivatives to describe anomalous nature of energy dissipation. Two model  
28 parameters were used for quantitative description of the rheological behaviour of the  
29 systems: the effective modulus and the dumping coefficient.

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

37

38 **Keywords:** Rheology, Mathematical modeling, Microstructure, Starch sodium octenyl  
39 succinate (OSA starch), Wheat flour dough

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**43 1. Introduction**

44

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

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

60 Beside cellulose, starch can also be chemically modified to become amphiphilic and thus  
61 can act as an effective emulsifier. Such emulsifying starch is octenyl succinate starch  
62 (OSA starch). There are a lot of advantages of using starch as raw material for  
63 modification. Beside cellulose it is most abundant naturally occurring polysaccharide  
64 available from plant kingdom. Moreover, it is characterized with low-cost,  
65 biocompatibility, biodegradability, non-toxicity, etc.

66 In contrast to emulsifying cellulose derivatives (Guarda et al., 2004; Lazaridou et al.,  
67 2007), there is very little information concerning the role of emulsifying starch in  
68 breadmaking. Taking into account the fact that other starch substitutes have exhibited  
69 significant bread improving properties in terms of crumb texture (Miyazaki et al., 2006)  
70 and that OSA starch has special nutritional values since it can act as functional fibre  
71 (Heacock et al., 2004) it is of a great importance to investigate the feasibility of OSA  
72 starch as bread improver.

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

81 Bread dough is a viscoelastic and shear thinning material combined of Hookean solid and  
82 non-Newtonian viscous liquid (Mirsaeedghazi et al., 2008). Various mechanical analogue  
83 models have been developed based on series and parallel combination of springs,  
84 dashpots and shear pins (Tanner et al., 2008). Some of them are difficult for analytical  
85 solving and light only parts of the complex phenomenon of dough rearrangement under  
86 various loading conditions. For deeper insight of the rheological response of the dough  
87 systems it is necessary to consider various types of interactions between the constituents  
88 on various spatial scales. Such interactions induce dumping effects in rheological

89 responses of the dough systems. Dumping effects should be connected with anomalous  
90 nature of energy dissipation and mathematically formulated by applying fractional  
91 derivatives (Podlubny, 1999; Metzler & Klafter, 2000).

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

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

104

## 105 **2. Materials and methods**

106

### 107 **2.1. Materials**

108

109 Wheat flour (12.9% moisture content, 11.9% protein, 0.64% ash) was obtained from the  
110 Fidelinka milling company AD, Serbia. Modified starches used in this study, provided by  
111 Cargill, France, included: non-physically modified starch sodium octenyl succinate

112 (C\*EmTex 06328), pregelatinized starch sodium octenyl succinate (C\*EmTex 12688)  
113 and hydrolyzed, spray-dried starch sodium octenyl succinate (C\*EmCap 12633). All  
114 three starches were modified waxy maize starches.

115

## 116 **2.2. Rheological measurements**

117

118 Rheological behaviour of OSA starch solutions and wheat flour doughs containing OSA  
119 starches in a concentration of 0, 5, 10, 15 and 20% was monitored with a HAAKE Mars  
120 rheometer (Thermo Scientific, Germany) at 30 °C.

121 Flow curves were monitored only for a) pregelatinized and b) hydrolyzed spray-dried  
122 OSA starches, since non-physically modified OSA starch was insoluble in cold water,  
123 and thus formed a suspension which particles settled down to the bottom of the cylinder,  
124 leading to sample inhomogeneity and measurement non-repeatability.

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

130 Dough was rheologically characterized with small deformation dynamic oscillatory tests.

131 The measurements were performed using parallel plate geometry (PP35S, 35 mm  
132 diameter) which was serrated in order to avoid slippage. The doughs for rheological  
133 experiments were prepared using a Mixolab (Chopin Technologies, France) mixing bowl.

134 The samples were kneaded at Mixolab water absorption (which was previously

135 determined as a percentage of water required for the dough to produce a torque of  
136  $1.1 \pm 0.05$  Nm), on 14% moisture basis. The following settings were used: mixing speed  
137 80 rpm, dough weight 75 g, tank temperature  $30^{\circ}\text{C}$ , mixing time was determined as a  
138 time required for dough to reach the consistency of 1.1 Nm (ranged from 2.5 to 5.5 min,  
139 depending on a sample). The dough was rested for 10 min in a closed plastic bag at  $30^{\circ}\text{C}$ .  
140 Subsequently, a sample was taken from the inner part of the dough, loaded between the  
141 plates and the gap adjusted to 1 mm. The excess material was removed with a spatula and  
142 the exposed sample edge was covered with a thin layer of light paraffin oil to prevent  
143 evaporation during measurements. The sample was rested between the plates for 10 min  
144 before testing to allow residual stresses to relax. Mechanical spectra (frequency sweeps)  
145 were recorded over the range 1–10 Hz at 2 Pa stress (which was within the linear  
146 viscoelastic region).

147

### 148 **2.3. Scanning Electron Microscopy (SEM)**

149

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



158

159 **2.4. Statistical analysis**

160

161 All samples were prepared and analyzed in triplicates and the results were reported as  
162 mean  $\pm$  standard deviation. Analysis of variance (ANOVA) followed by Tukey test with  
163 0.05 significance level were used to assess significant differences among the means.  
164 ANOVA was carried out with the Statistica 10 (StatSoft Inc., USA).

165

166 **3. Model development**

167

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

181 between the opposite charged segments which tend to keep the structural integrity and  
 182 cause the damping of energy dissipation. The damping effects should be connected with  
 183 the non-linear nature of the systems rheological responses.

184 Deeper insight into the non-linear rheological responses is necessary for improving the  
 185 rheological and nutritional performances of the examined systems. Consequently, we  
 186 model the intrinsic dynamics of the dough structural rearrangement by applying the  
 187 internal variable theory in one side and introducing the fractional derivatives in the other.  
 188 The internal variable theory has been used for describing the impact of energy dissipation  
 189 on various system rheological responses (Coleman and Gurtin, 1967; Trumel et al., 2001;  
 190 Atanackovic, 2002). On that base, the state of the systems is described by the total shear  
 191 strain component  $\gamma(t)$  and the internal variable  $\xi(t)$  as well as by the specific  
 192 thermodynamics variables. The specific thermodynamic variables as:  $u(t)$  the internal  
 193 energy,  $s(t)$  the entropy and the Helmholtz free energy  $u(t) - T s(t)$  depends on the total  
 194 shear strain component  $\gamma(t)$  and the internal variable  $\xi(t)$ . The internal variable  
 195 represents the irreversible part of the total shear strain.

196 The main task in the lighting of the dissipative phenomena is the postulating of the  
 197 relationship between the total shear strain component  $\gamma(t)$  and its irreversible part  $\xi(t)$   
 198 and further verification of the assumption by comparing model prediction with  
 199 experimental data. We assume that changes of the total shear strain component  
 200 simultaneously induce changes of its irreversible part in the form:  ${}_0D_t^\alpha(\gamma(t)) \approx {}_0D_t^\alpha(\xi(t))$

201 (where  ${}_0D_t^\alpha(\bullet) = \frac{d^\alpha}{dt^\alpha}(\bullet)$  is the fractional derivative of some function). Reversible part of

202 the total shear strain component increases more rapidly up to its maximum value and stay

203 approximately constant during experimental time period. For this condition, the changes  
 204 of the specific Helmholtz free energy under isothermal conditions could be expressed as:

$$205 \quad \rho \, {}_0D_t^\alpha (u(t) - T s(t)) = (\sigma_T(t) - \Theta(t)) D_t^\alpha (\gamma(t)) \quad (1)$$

206 where  $\rho$  is the system averaged density,  $\sigma_T(t)$  is the component of total shear stress,

207  $\Theta(t)$  is the component of the irreversible part of the stress,  ${}_0D_t^\alpha (f(t)) = \frac{d^\alpha}{dt^\alpha} (f(t))$  is the

208 fractional derivative of some function  $f(t)$  while  $\alpha$  is the order of the fractional

209 derivatives (the dumping coefficient). Caputo's definition of the fractional derivative of a

210 function  $f(t)$ , was used and it is given as follows (Podlubny, 1999):

$$211 \quad {}_0D_t^\alpha (f(t)) = \frac{1}{\Gamma(1-\alpha)} \frac{d}{dt} \int_0^t \frac{f(t')}{(t-t')^\alpha} dt' \quad (2)$$

212 where  $t$  is an independent variable (time) and  $\Gamma(1-\alpha)$  is the gamma function. If

213 parameter  $\alpha$  is  $\alpha = 0$ , we obtain  ${}_0D_t^0 (f(t)) = f(t)$ . When  $\alpha = 1$ , the corresponding gamma

214 function  $\Gamma(1-\alpha) \rightarrow \infty$ . For this case, the fractional derivative is not defined. However, it

215 can be shown, that in the limit when  $\alpha \rightarrow 1$ , follows  ${}_0D_t^\alpha (f(t)) \rightarrow \dot{f}(t)$ , where the dot

216 denotes the first time derivative. Thus, when  $0 \leq \alpha < 1$ , the equation 1 describes the

217 dumped dissipative phenomena. Smaller value of the parameter  $\alpha$  points to more

218 pronounced dumping effects.

219 It was assumed that the component of total shear stress  $\sigma_T(t)$  and the component of the

220 irreversible part of stress  $\Theta(t)$  represent the linear functions of the variables  $\gamma(t)$  and

221  $\xi(t)$ . Non-linear nature of the systems rheology is connected with the dumping effects.

222 The component of total shear stress  $\sigma_T(t)$  and the component of the irreversible part of  
 223 stress  $\Theta(t)$  are expressed as:

$$224 \quad \sigma_T(t) = \kappa_1 \gamma(t) + \kappa_2 \xi(t) \quad \text{and}$$

$$225 \quad \Theta(t) = \beta_1 \gamma(t) + \beta_2 \xi(t) \quad (3)$$

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

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

$$233 \quad \rho {}_0 D_t^\alpha (u(t)) = \rho D_t^\alpha (Q(t)) + \sigma_T(t) {}_0 D_t^\alpha (\gamma(t)) \quad (4)$$

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

$$237 \quad {}_0 D_t^\alpha (s(t)) = \frac{1}{T} D_t^\alpha (Q(t)) + {}_0 D_t^\alpha (s_i(t)) \quad (5)$$

238 where  ${}_0 D_t^\alpha (s(t))$  represents the total production of entropy while  ${}_0 D_t^\alpha (s_i(t))$  represents  
 239 the internal production of entropy which satisfy condition  ${}_0 D_t^\alpha (s_i(t)) \geq 0$  for irreversible  
 240 processes. The internal production of entropy during rearrangement of dough systems is  
 241 determined after introducing eqs. 4 and 5 into eq. 1. It is expressed as:

$$242 \quad \rho {}_0 D_t^\alpha (s_i(t)) = \frac{\Theta(t)}{T} {}_0 D_t^\alpha (\gamma(t)) \geq 0 \quad (6)$$

243 We have indicated that the entropy production is positive. The inequality 6 may be  
 244 satisfied by setting:

$$245 \quad \Theta(t) = \psi {}_0D_t^\alpha(\gamma(t)) \quad (7)$$

246 where  $\psi$  is the modulus which quantified the irreversible phenomenon caused by  
 247 changes the component of the total shear strain.

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

$$251 \quad \sigma_T(t) = G_s \gamma(t) + \eta {}_0D_t^\alpha(\gamma(t)) \quad (8)$$

252 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

253 effective modulus equal to  $\eta = \psi \frac{\kappa_2}{\beta_2}$ . The static modulus combines the reversible and

254 irreversible parts of the phenomenon. However, the effective modulus represents the

255 measure of local irreversible processes of the systems structural organization. The first

256 term of the right hand side of eq. 8 represents the reversible (elastic) part and the second

257 term represents the irreversible (viscous) part of the component of total stress. If the

258 parameter  $\alpha$  is  $\alpha = 0$ , we obtain  ${}_0D_t^0(\gamma(t)) = \gamma(t)$ . For such case the second term of eq. 8

259 additionally contributes to elastic Hookean behaviour. When  $\alpha \rightarrow 1$ , we obtain

260  ${}_0D_t^\alpha(\gamma(t)) \rightarrow \dot{\gamma}(t)$ . For such case, the second term represents the purely viscous

261 contribution to the total stress.

262 Development constitutive model equation proposed for describe the rearrangement of the

263 dough systems is the modified to Kelvin-Voigt type model with fractional derivatives.

264 Various fractional forms of Kelvin-Voigt model have been used for describing non-linear  
 265 responses of viscoelastic solid systems (Djordjevic et al, 2003). However, little has been  
 266 reported about the corresponding intrinsic dynamics of the systems rearrangement which  
 267 represents the course of the non-linear response.

268 Eq. 8 was transformed from the time domain into the frequency domain using the Fourier  
 269 integral transform. Transforming equation is expressed in the form  
 270  $F[\sigma_T(t)] = G^* F[\gamma(t)]$ , where  $F[\circ]$  is the Fourier operator and  $G^*$  is the complex  
 271 dynamic modulus equal to  $G^* = G' + iG''$ , while  $G'$  is the storage modulus and  $G''$  is the  
 272 loss modulus and  $i = \sqrt{-1}$  is the imaginary unit. Fourier transform of the fractional  
 273 derivative of the component of shear strain  $\gamma(t)$  is expressed as  
 274  $F[{}_0D_t^\alpha(\gamma(t))] = (i\omega)^\alpha F[\gamma(t)]$ , where  $\omega$  is the angular frequency (Djordjevic et al, 2003).

275 The storage and loss moduli are expressed as:

$$276 \quad G'(\omega) = G_s + \eta\omega^\alpha \cos\left(\frac{\pi\alpha}{2}\right)$$

$$277 \quad G''(\omega) = \eta\omega^\alpha \sin\left(\frac{\pi\alpha}{2}\right) \quad (9)$$

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

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

284

**285 4. Results and discussion**

286

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

305 Rheological behaviour of the systems with additions of the OSA starches also depended  
306 on rigidity of OSA starch granules themselves. Rigidity could be correlated with ability

307 to water absorption. The ability to water absorption depended on: ordering of  
308 amylopectin chains and chain molecular weight distribution.

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

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

319 Higher water absorption of the systems with addition of the pregelatinized OSA starches  
320 as compared to the non-physically modified OSA starch represented the consequence of  
321 amorphous, more open porous structure of the pregelatinized OSA starches (Table 1).  
322 However, addition of the hydrolyzed spray-dried OSA starch induced decrease of dough  
323 water absorption as compared to the control system. Enzymatic hydrolysis of  
324 amylopectin chains caused decrease in amylopectin molecular weight and thus lower  
325 ability to water absorption of these granules.

326 In order to estimate the morphological characteristics of physically modified OSA  
327 starches, flow curves of 5% cold water solutions of: the pregelatinized OSA starches and  
328 the hydrolyzed spray-dried OSA starch were monitored (Figure 2). The viscosity of the  
329 5% hydrolyzed spray-dried OSA starch water solution was much lower than the viscosity



330 of the 5% pregelatinized OSA starch water solution. It was in accordance with the facts  
331 that averaged molecular weight of amylopectin molecules was much lower in the case of  
332 the hydrolyzed spray-dried OSA starches.

333 Rheological behaviour of the systems with the addition of various OSA starch granules  
334 was considered under oscillatory strain conditions. The predicted values of the moduli  
335 were calculated using constitutive eq. 9.

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

351 As shown in Figure 4 A-B, the model prediction values for the dough systems with  
352 various amounts of the pregelatinized OSA starch (Figure 1 D) correlated well with the

353 one representative corresponding experimental set, with relative error of 10%. The  
354 optimal model parameters obtained by this fitting procedure that enable the best  
355 comparison with the experimental data where shown in Table 2. Addition of various  
356 amounts of the pregelatinized OSA starch granules induced softening of the dough  
357 systems. It was in accordance with the fact that: (1) the effective external surface of the  
358 pregelatinized OSA starch granules was the smallest and (2) the technological treatment  
359 of formation the pregelatinized OSA starch granules led to the granule crystalline  
360 structure destruction. A higher degree of macromolecular disorganization led to higher  
361 solubility of these starches which formed viscous pseudoplastic systems (Figure 2).  
362 Therefore, in dough these OSA starches increased water absorption (Table 1). Due to loss  
363 crystallinity and higher amount of water in the system pregelatinized OSA starch yielded  
364 softer, stickier and weaker dough systems in comparison to control, in which gluten  
365 structural continuity was affected (Figure 1 E).

366 As shown in Figure 5 A-B, the model prediction values for the dough systems with  
367 various amounts of the hydrolyzed spray-dried OSA starch granules (Figure 1 F)  
368 correlated well with the one representative corresponding experimental set, with relative  
369 error of 10%. The optimal model parameters obtained by this fitting procedure that  
370 enable the best comparison with the experimental data where shown in Table 2. Addition  
371 of various amounts of the hydrolyzed spray-dried OSA starch granules also induced  
372 softening of the dough systems. The softening in such case was not so pronounced as for  
373 the systems with additions of the pregelatinized OSA starch granules. It represented the  
374 consequence of low ability to water absorption of hydrolyzed amylopectin chains.  
375 Hydrolysis led to decrease of the molecular weight and consequently to decrease in

376 solution viscosity (Figure 2). Low amount of water induced formation of more rigid  
377 structure as compared to the system containing pregelatinized OSA granules. However,  
378 the hydrolyzed spray-dried OSA granules were significantly softer than the non-  
379 physically modified OSA starch granules due to: (1) amorphous structure and (2) low  
380 molecular weight of amylopectin chains. Therefore, when added to wheat flour, these  
381 starches decreased flour water absorption (Table 1) and yielded the dough of weakened  
382 structure (Figure 1 G).

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

392 The mean values of the model parameters and the corresponding standard deviations,  
393 shown in Table 2, were determined by comparing the model predictions with the three  
394 repeated experimental sets for every experimental condition. The dough systems  
395 notations were: a) the non-physically modified, b) the pregelatinized and c) the  
396 hydrolyzed spray-dried OSA starch granules. The notations were the same as in the  
397 Figures 3-5 (A, B).

398 The effective modulus  $\eta$  (Table 2) increased with the increase in the amount of non-  
399 physically modified OSA starch granules (Figure 1 B). It quantified increase of the  
400 system rigidity due: rigidity of added non-physically modified OSA starch granules and  
401 increased density of non covalent bonds. At the same time, the dumping coefficient  
402  $\alpha$  decrease as the results of increase in the density of non covalent bonds. These systems  
403 showed lower ability of adaptation to oscillatory strain condition with pronounced  
404 dumping effects. However, the addition of the pregelatinized and the hydrolyzed spray-  
405 dried OSA starch granules (Figure 1 D and F) induced decrease of the effective modulus  
406  $\eta$  with increase in the amount of OSA starch. It represented the consequence of addition  
407 of OSA granules with weakened or destroyed crystalline structures responsible for the  
408 integrity of the granule. At the same time, the softening of these systems was quantified  
409 by higher values of the dumping coefficient  $\alpha$ . The relation between the effective  
410 modulus and the dumping coefficient could be expressed as:  $\eta \sim \alpha^{-1}$ .

411

## 412 5. Conclusions

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414 Addition of various types of OSA starch granules (the non-physically modified, the  
415 pregelatinized and the hydrolyzed spray-dried) to the wheat dough systems significantly  
416 influenced the system rheological behaviour. It primarily depends on the rigidity of added  
417 OSA starch granules and their effective external surfaces. Higher effective surfaces  
418 induced higher density of hydrophilic and hydrophobic bonds between the system  
419 constituents. Consequently, addition of various amounts of the non-physically modified  
420 OSA starch granules induces the system reinforcement. On the other side, addition of

421 various amounts of the pregelatinized and the hydrolyzed spray-dried OSA starch  
422 granules induces the system softening.

423 Rheological behaviour of the examined system is described based on the developed  
424 model by introducing the assumption that changes of the total shear strain component  
425 simultaneously induce changes of its irreversible part while the reversible part more  
426 rapidly reaches its maximum value. The results points to anomalous dissipation of energy  
427 due to the system rearrangement as the dominant mechanism of their responses to  
428 oscillatory strain conditions. Anomalous mechanism is quantified by introducing the  
429 fractional derivatives and the dumping coefficient  $\alpha$  on one side and the effective  
430 modulus  $\eta$  on the other.

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

440

441 **Acknowledgements.** The support by grants (III 46001 and III 46010) from the Ministry  
442 of education, science and technological development, Republic of Serbia is gratefully  
443 acknowledged.

444

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494 **Figure captions**

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

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

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

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

507 **Fig. 5 A-B.** Storage (A) and loss (B) moduli as a function of frequency for the dough  
508 system with addition of the 0-20 % of the hydrolyzed spray-dried OSA starch (the dough  
509 system noted as c)

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517 **Table 1.** Mixolab water absorption values of control dough and doughs containing OSA  
 518 starches in different concentrations

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

519 Values followed by the same letter in the column are not significantly different ( $p > 0.05$ )

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532 **Table 2.** The model parameters

Dough systems	$\alpha$ (-)	$\eta$ (Pa s $^\alpha$ )
Control-0% OSA starch	0.225±0.01 <sup>b</sup>	(0.70±0.01 <sup>g</sup> )x10 <sup>4</sup>
Non-physically modified OSA starch (a)		
5 %	0.190±0.01 <sup>a</sup>	(1.00±0.01 <sup>h</sup> )x10 <sup>4</sup>
10 %	0.187±0.01 <sup>a</sup>	(1.35±0.01 <sup>i</sup> )x10 <sup>4</sup>
15 %	0.186±0.01 <sup>a</sup>	(1.50±0.01 <sup>j</sup> )x10 <sup>4</sup>
20 %	0.185±0.01 <sup>a</sup>	(1.56±0.01 <sup>k</sup> )x10 <sup>4</sup>
Pregelatinized OSA starch (b)		
5 %	0.245±0.01 <sup>b</sup>	(0.46±0.01 <sup>e</sup> )x10 <sup>4</sup>
10 %	0.250±0.01 <sup>b</sup>	(0.33±0.01 <sup>c</sup> )x10 <sup>4</sup>
15 %	0.320±0.01 <sup>d</sup>	(0.13±0.01 <sup>a</sup> )x10 <sup>4</sup>
20 %	0.340±0.01 <sup>d</sup>	(0.11±0.01 <sup>a</sup> )x10 <sup>4</sup>
Hydrolyzed spray-dried OSA starch (c)		
5 %	0.230±0.01 <sup>b</sup>	(0.70±0.01 <sup>g</sup> )x10 <sup>4</sup>
10 %	0.235±0.01 <sup>b</sup>	(0.55±0.01 <sup>f</sup> )x10 <sup>4</sup>
15 %	0.240±0.01 <sup>b</sup>	(0.39±0.01 <sup>d</sup> )x10 <sup>4</sup>
20 %	0.290±0.01 <sup>c</sup>	(0.23±0.01 <sup>b</sup> )x10 <sup>4</sup>

533 Values followed by the same letter in the column are not significantly different (p &gt; 0.05)

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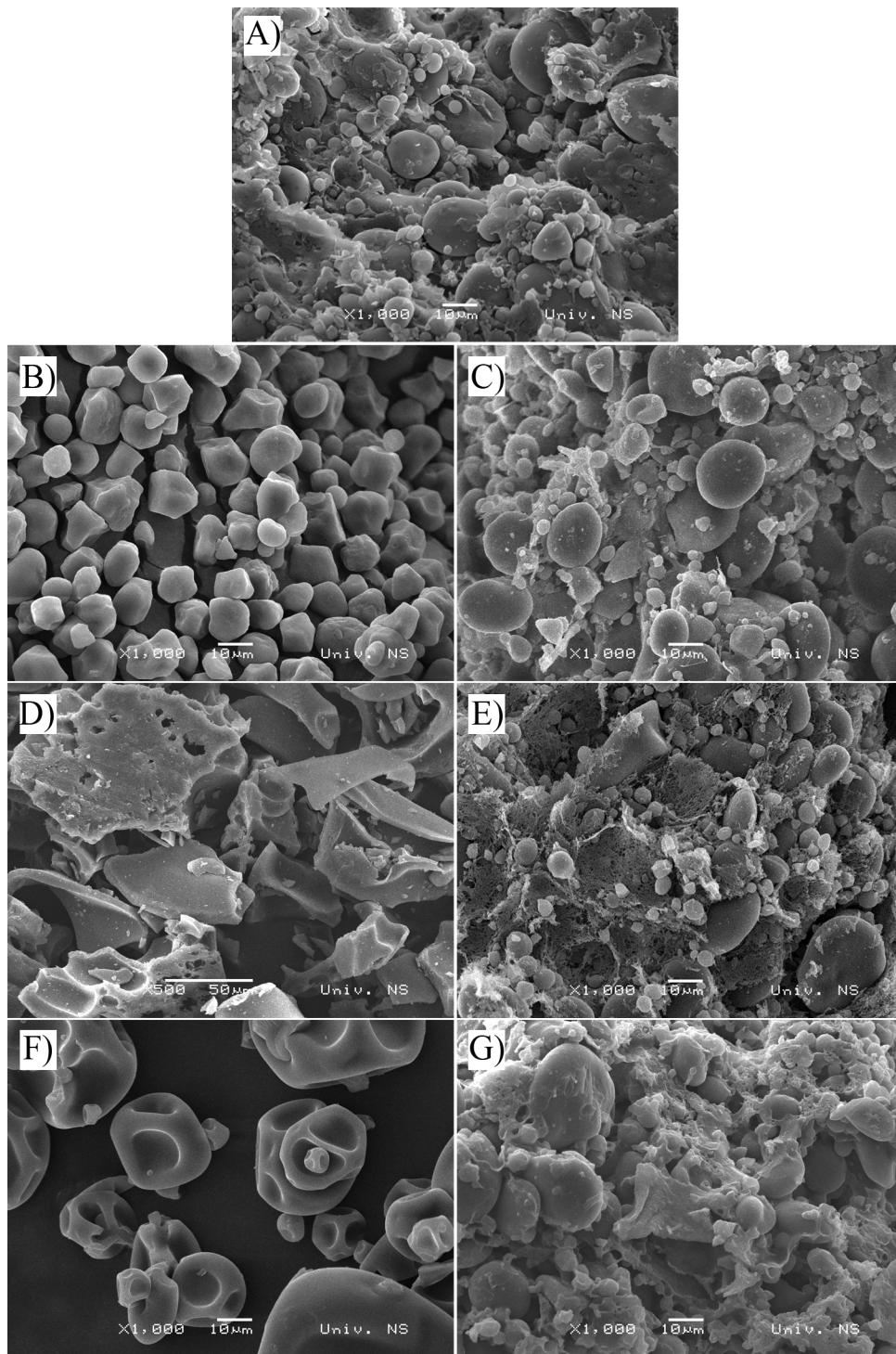
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547 **Fig. 1 A-G**

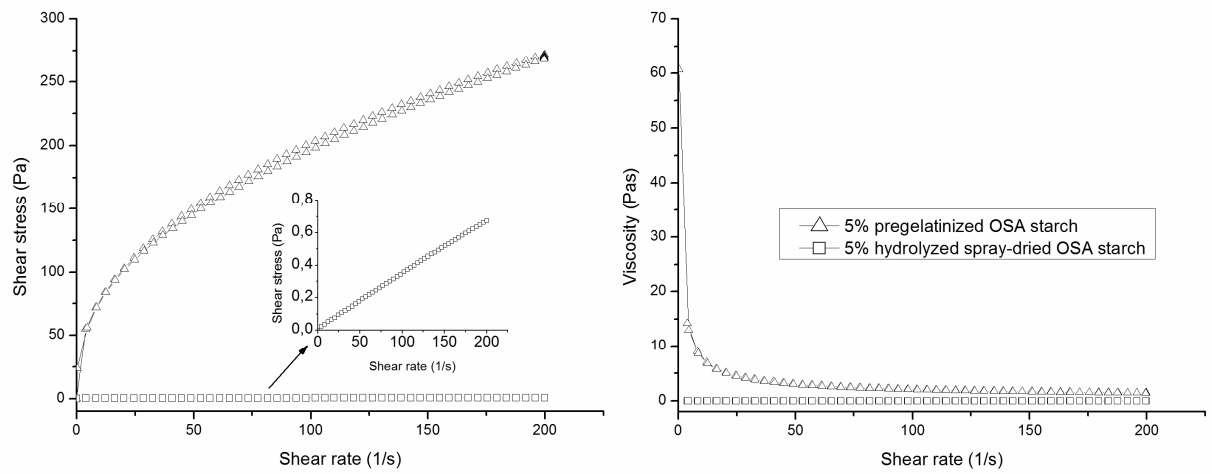


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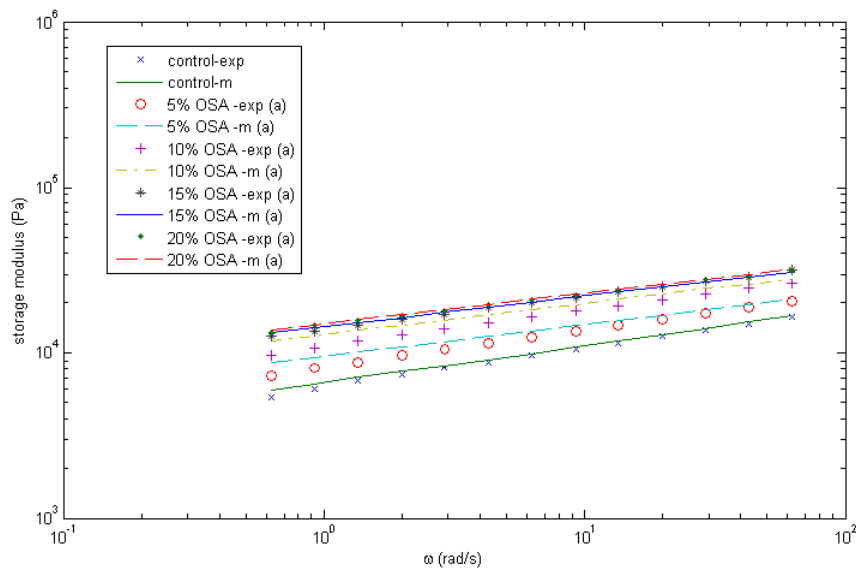
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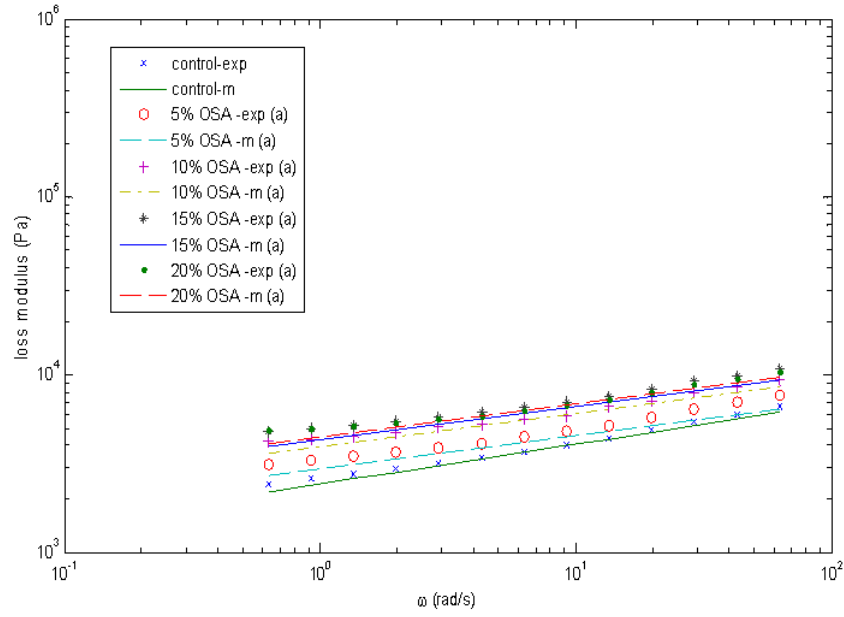


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553 **Fig. 3 A-B**

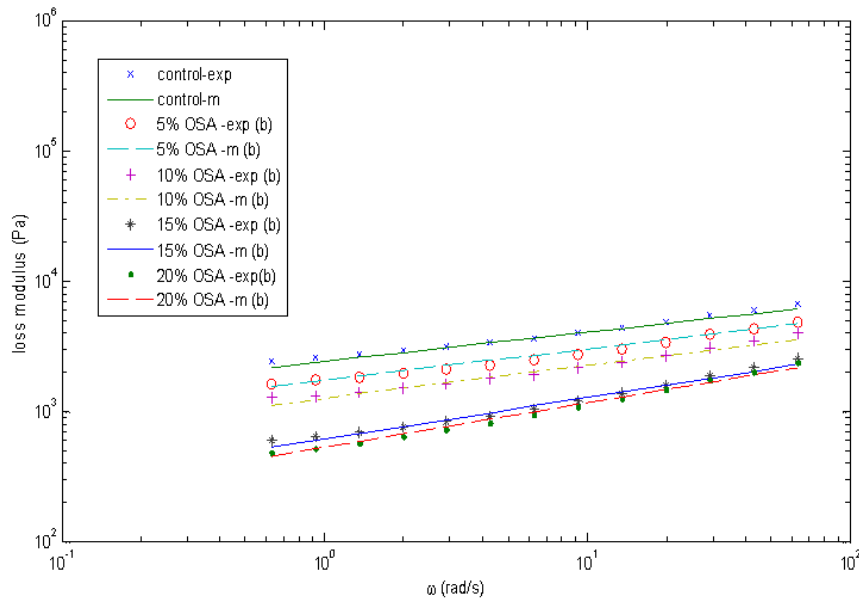


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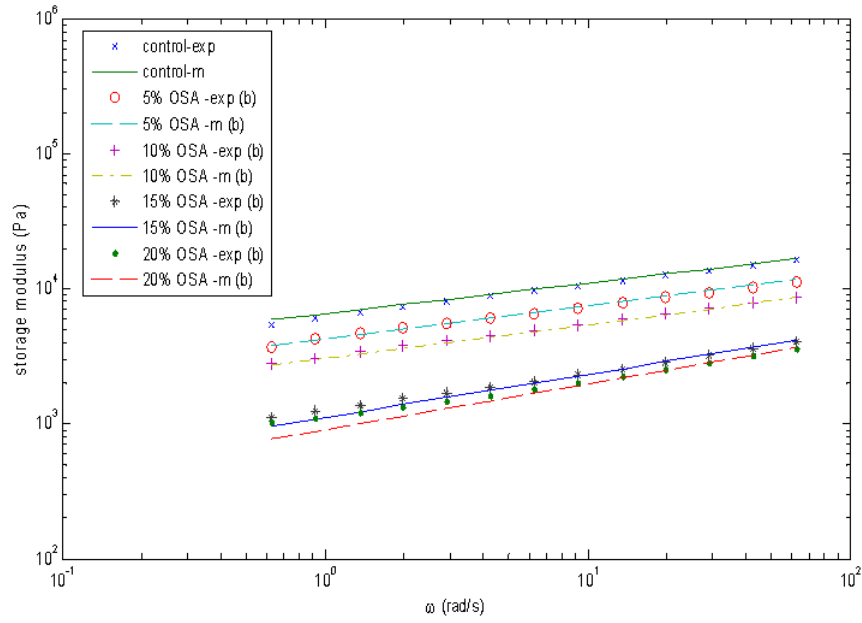


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556 **Fig. 4 A-B**

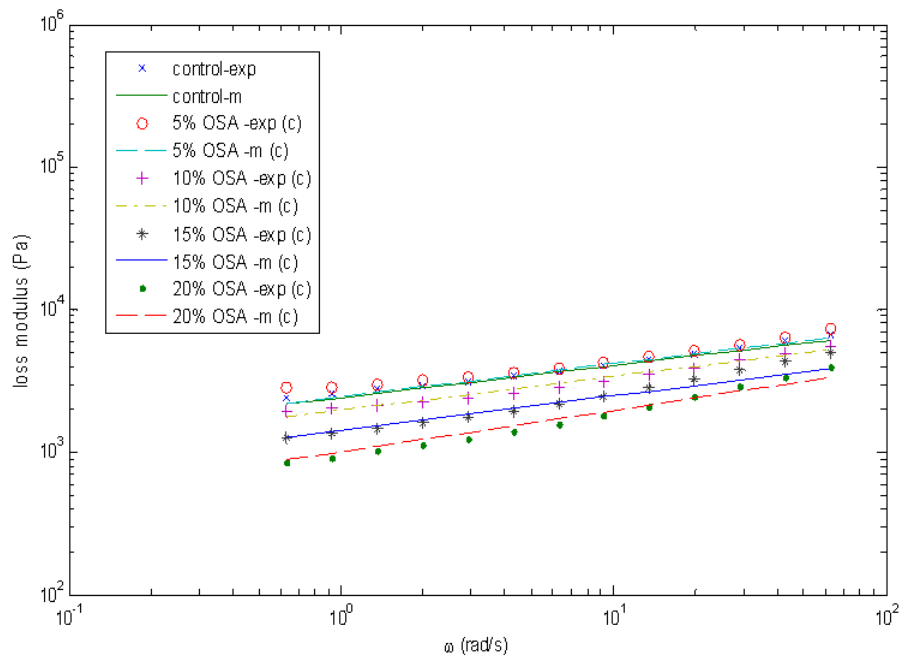


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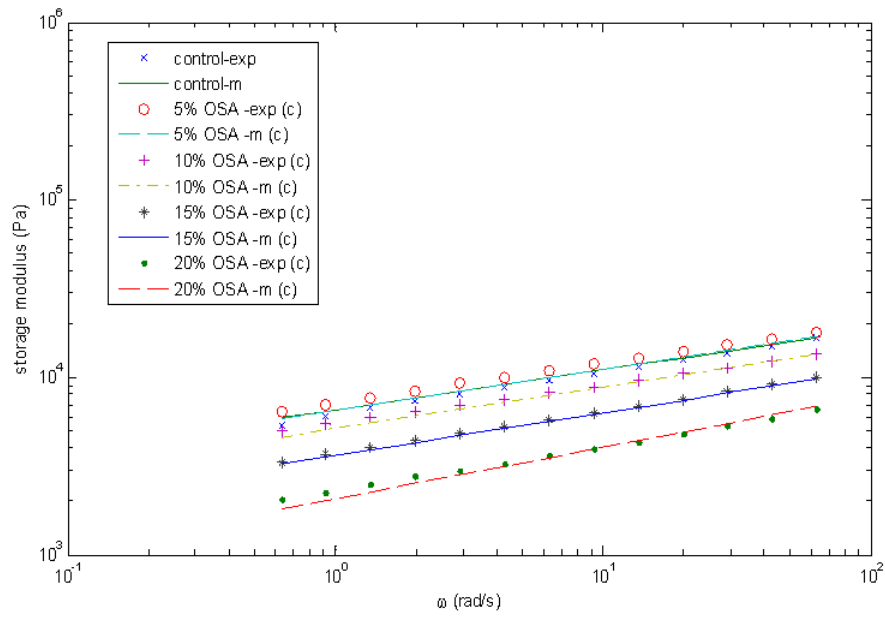


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559 **Fig. 5 A-B.**



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