STRUCTURAL MECHANICAL AND GELLING PROPERTIES OF ALGINATE BEADS

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Abstract

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The present research is dedicated to the formation of alginate beads from sodium alginate, calcium salts and sucrose. Sodium alginate solutions in 30 g.kg^{-1} and 60 g.kg^{-1} concentrations, with calcium chloride dihydrate in 40 g.kg^{-1} and 70 g.kg^{-1} concentrations and with sucrose in 650 g.kg^{-1} concentration were used for bead formation. The highest rupture strength was received for the 60 g.kg^{-1} sodium alginate beads standing in 200 g.kg^{-1} calcium chloride dihydrate solution for 3 hours. The weakest beads were obtained from the combination of 30 g.kg^{-1} sodium alginate, 40 g.kg^{-1} calcium lactate and 650 g.kg^{-1} sucrose. It was shown that the most elastic beads were obtained from the combination of 60 g.kg^{-1} sodium alginate and 100 g.kg^{-1} calcium chloride dihydrate and the less elastic beads were received from the combination of 30 g.kg^{-1} sodium alginate standing in 40 g.kg^{-1} calcium lactate solution for 1 or 2 hours. The rupture force and rupture deformation is growing/decreasing with increasing of gelling time. The beads obtained have pleasant taste and colour. They can be used for artificial fruit formation in the confectionary industry in manufacture of ice cream and cocktails.

Key words: alginate beds, gelling properties, confectionary industry

Introduction

Alginic acid is a major component in cell wall of brown algae and is received from over there. The alginic acid has two monomer units, namely β-D- mannopyranuronate and α-L- gulopyranuronate (Figure 1) (Vos et al., 2006).

The β-D-mannuronic acid is more stable than α-L- gulopyranuronate because the β-D- mannopyranuronate in alginic acid is in $^4C_1$ conformation where there is no spatial interaction between the groups, while the α-L- gulopyranuronate has spatial interaction between the axially situated COOH-group at C_5 and OH-group at C_3 of α-L- gulopyra-

nuronate. These two acids are the main uronic monomer units in the alginic acid molecule, with different types of connections. The uronoic acid form is a series of structural monomer units from MMMMM, GGGGG or MGMGMGMG (Grasdalen et al., 1981; Haug et al., 1966; Haug et al, 1974). The alginates are Na, Ca, K and Mg salts of alginic acid in marine algae. The Ca salt is insoluble in water. The Na-alginate is used as a gelling agent for nutritional purposes. The gelling force depends on the β-D- mannopyranuronate and α-L- gulopyranuronate ratio. The gelling ability is greater at smaller ratio (Kloareg and Quatrano, 1988; Perez et al., 1992). Jelly structures for food are formed from alginic acid in the presence of multivalent ions (Ca^{2+}), because these ions are less toxic (Nussinovitch, 1997). Calcium chloride dihydrate or Ca lactate are used like ion sources. The pure alginic acid is hard to dissolve in cold water, while swells in it, 200-300 times. It easily dissolves in hot water and forms gel by acidification in the presence of calcium ions. The carboxyl groups with alginic acid form alginates by neutralization (sodium, potassium). These are soluble also in hot and cold water and form solutions with high viscosity. Alginates act
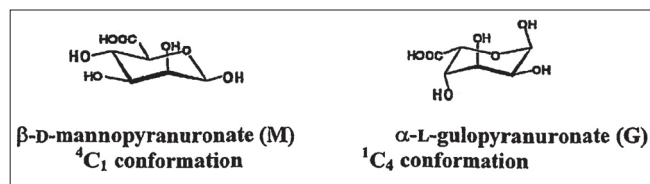

Fig. 1. Monomers of the alginic acid: β-D- mannopyranuronate (M) (left) α-L- gulopyranuronate (G) (right)
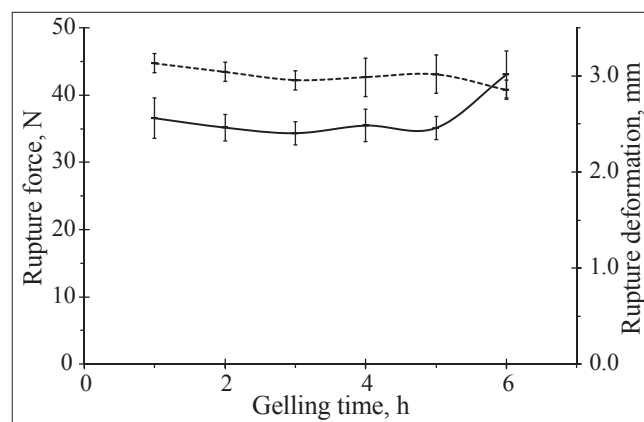
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as thickeners, emulsifiers and gel forming agent. Calcium alginate destroys the foam. One of the major advantages of the alginates is their ability to form gel that is stable both at low and high temperatures. Therefore, the properties of the alginate gels do not depend on temperature. It is found that the gels formed in the presence of calcium lactate, like those with calcium chloride, are independent on the temperature and pH of the surrounding environment. The addition of calcium chloride to the solution of sodium alginate is caused instant gel formation. That gel cannot be homogenised even at high speed stirring, because they fast form very strong and irreversible jelly nodes and thus achieves higher rate of gelation (Draget et al., 2006). It was experimentally found that the addition of calcium salt to Na-alginate provokes instant gelling, which is irreversible due to the cooperation of calcium ions with α-L- gulopyranuronate. As a result 3-D structure, called 'egg box', is obtained (Rousseau et al., 2004). The egg box structure forming time (gelling time) depends on the calcium salt, temperature and pH of the me-

dium. The shortest gelling time (3 min) was estimated with calcium lactate at 20°C and the longest (more than 3 days) with calcium carbonate at 60°C. The gel strength depends on the calcium salt concentration of alginate, on the time and on the temperature. It is also found that in at low pH environment gel formation time is shorter. Destabilization of the jellies is obtained at very low or very high pH values because of the increasing rate of depolymerization processes, such as a proton-catalyzed hydrolysis of jelly and α-elimination (Smidsrod and Draget, 1997). About 7.2% (w/w) calcium ions, based on the weight of sodium alginate, was stoichiometrically required for complete gelation (Lu Ren, 2008). The greatest amount of calcium ions released with calcium carbonate – 400.4 g.kg^{-1} Ca^{2+}, and the less with calcium citrate – 70.3 g.kg^{-1} Ca^{2+}.
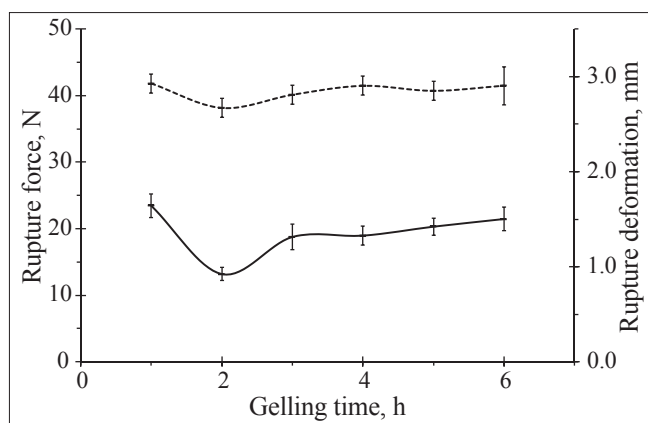
The aim of this study was to characterize the gel strength of alginate beads by rheological method – Determination of rupture strength of the gel under uni-axial compressive strain.
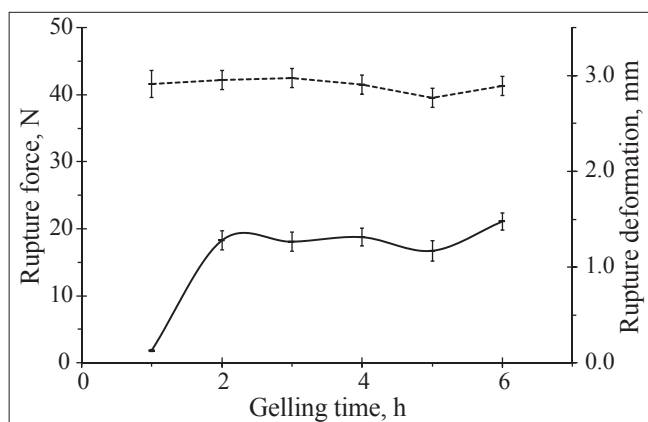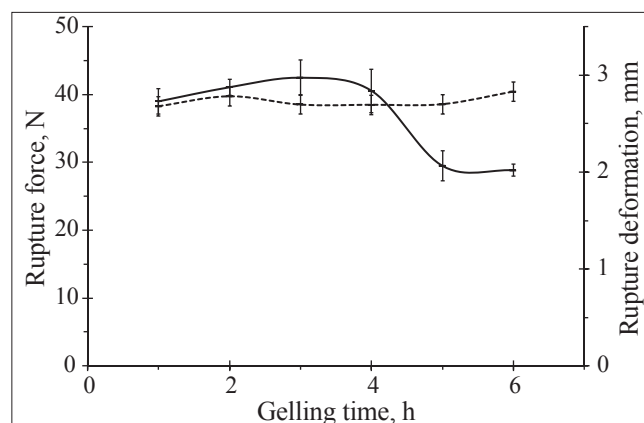

a) 30 g.kg^{-1} Na-alg. + 100 g.kg^{-1} CaCl$_2$ x 2 H$_2$O
b) 60 g.kg^{-1} Na-alg. + 100 g.kg^{-1} CaCl$_2$ x 2 H$_2$O
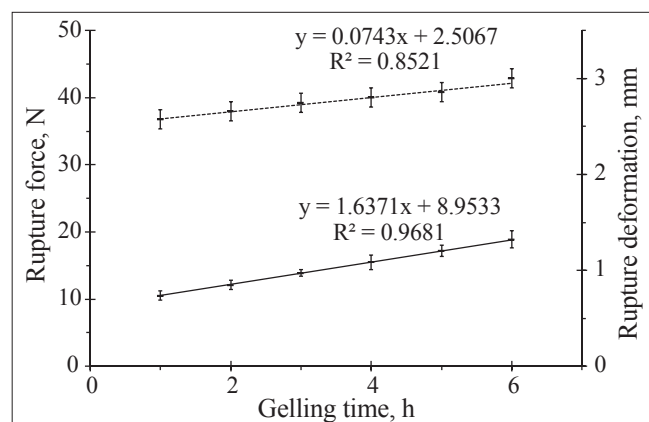c) 30 g.kg^{-1} Na-alg. + 200 g.kg^{-1} CaCl$_2$ x 2 H$_2$O
d) 60 g.kg^{-1} Na-alg. + 200 g/kg^{-1} CaCl$_2$ x 2 H$_2$O

Fig. 2. Rupture force (——) and deformation (- - -) in function of gelling time for sodium alginate with calcium salts

The staff of the paper has analogous study of the influence of crosslinking agent on the process of gelling low-esterified pectin (Marudova et al., 2009) and study the formation of multilayer beads from chitosan and kappa-carrageenan in the precipitation bath of sodium hydroxide (Marudova and Zsivanovits, 2009).

Materials and Methods

Stable Micro Systems TA.XT Plus texture analyser was used for gel strength investigation of alginate beads. The rupture force obtained from force-deformation curve was compared for the different samples. 30 g.kg⁻¹ and 60 g.kg⁻¹ Na-alginate (technically pure), 40 g.kg⁻¹ and 7 g.kg⁻¹ calcium lactate pentahydrate (chemically pure), 10 g.kg⁻¹ and 20 g.kg⁻¹ calcium chloridedihydrate and 650 g.kg⁻¹ % sucrose (technically pure) was used for receiving the alginate beads. 1-6 hours gelling time series (steps 1 hour) was used at room temperature for analyzing the time dependency of gel forming.
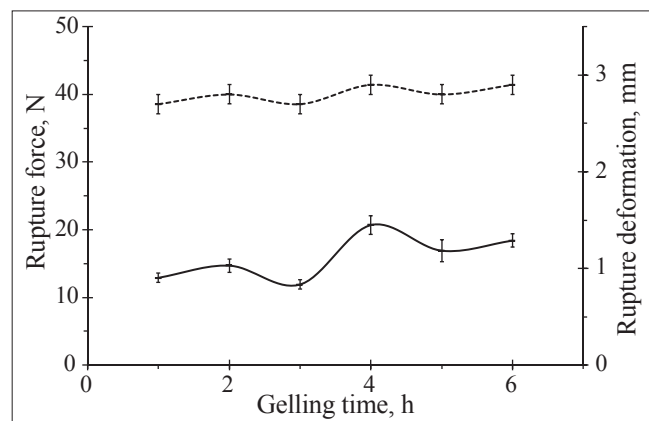
Results

Figure 2 a-d show the change of rupture force and deformation as a function of gelling. Figure 3 a-d show the change of rupture force and deformation as a function of gelling time of Na-alginate beads with calcium lactate pentahydrate. Both the rupture force and the rupture deformation are growing with increasing of gelling time at 30 g.kg⁻¹ Na-alg. + 40 g.kg⁻¹ $C_6H_{10}O_6Ca$ (Figure 3a). The rupture deformation is constant only at the 60 g.kg⁻¹ Na-alg. + 40 g.kg⁻¹ $C_6H_{10}O_6Ca$ (Figure 3b).

Figure 4 a-d show the change of rupture force and deformation in function of gelling time of Na-alginate beads with calcium lactate pentahydrate and sucrose.

Figure 5 shows the changing of rupture force and deformation as a function of calcium dichloride concentration at fixed gelling time and Na-alginate concentration. The rupture deformation is decreasing at 60 g.kg⁻¹ Na-alg. after 3 hours gelling (Figure 5) with increasing of $CaCl_2$ concentration.
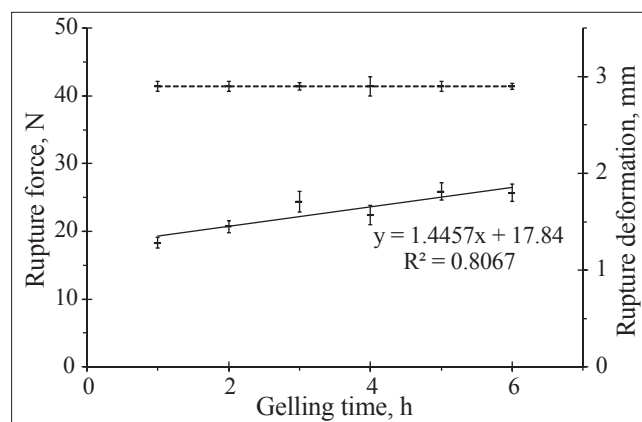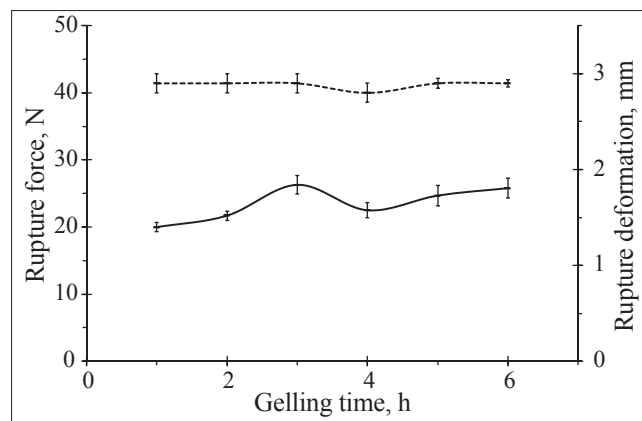
a) 30 g.kg⁻¹ Na-alg. + 40 g.kg⁻¹ $C_6H_{10}O_6Ca$
b) 60 g.kg⁻¹ Na-alg. + 40 g.kg⁻¹ $C_6H_{10}O_6Ca$
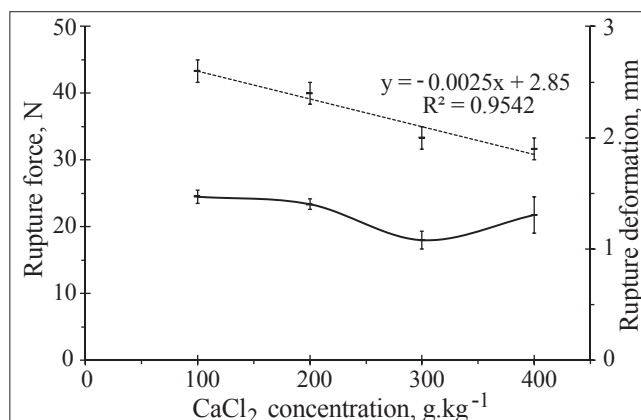c) 30 g.kg⁻¹ Na-alg. + 70 g.kg⁻¹ $C_6H_{10}O_6Ca$
d) 60 g.kg⁻¹ Na-alg. + 70 g.kg⁻¹ $C_6H_{10}O_6Ca$

Fig. 3. Rupture force (——) and deformation (- - -) in function of gelling time for sodium alginate with calcium-lactate

Conclusions

- The highest rupture force (43.1 N) was received for beads with 60 g.kg^{-1} Na-alginate and with 100 g.kg^{-1} calcium chloride dihydrate after 6 hours gelling time and the lowest (4.3 N) for beads with 30 g.kg^{-1} Na-alginate, with 70 g.kg^{-1} calcium lactate and with 650 g.kg^{-1} sucrose after 1 hours gelling time.
- The highest deformation at the rupture point (3.1 mm) was measured for beads, combination of 60 g.kg^{-1} sodium alginate with 10 g.kg^{-1} calcium chloride dihydrate after 1-hour gelling time. The smallest one (2.2 mm) was detected for beads, combination of 30 g.kg^{-1} sodium alginate with 40 g.kg^{-1} calcium lactate pentahydrate and with 650 g.kg^{-1} sucrose after 4 hours gelling time and beads, combination of 3 g.kg^{-1} sodium alginate with 70 g.kg^{-1} calcium lactate pentahydrate and with 650 g.kg^{-1} sucrose after 5 hours gelling time.
- The increase of CaCl$_2$ concentration at a particular constant alginate concentration and gelation time leads to decrease of rupture deformation.
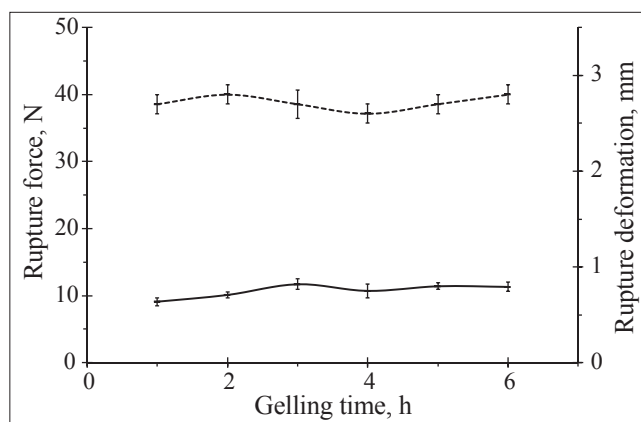
- Based on our experiment series the greatest decreasing in the rupture force was seen because of added sucrose. Between
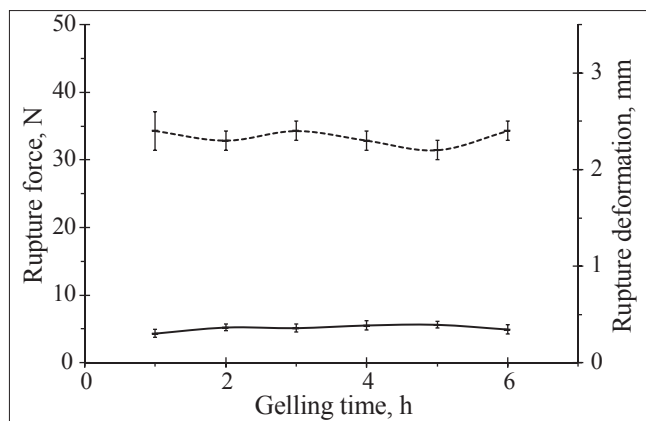

Fig. 5. Rupture force (——) and deformation (- - -) in function of calcium salt concentration at fixed gelling time (3 hours) for 60 g.kg^{-1} sodium alginate
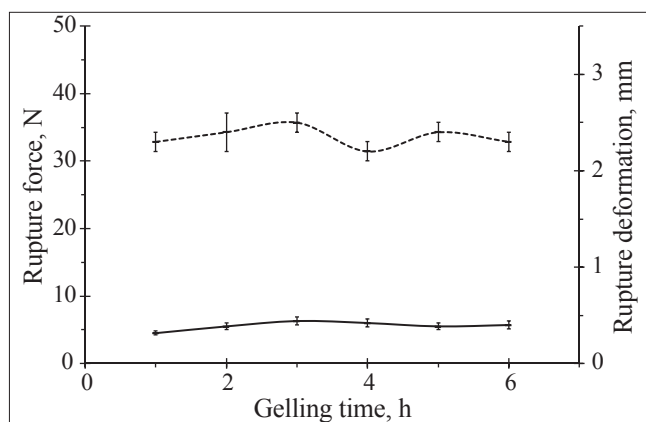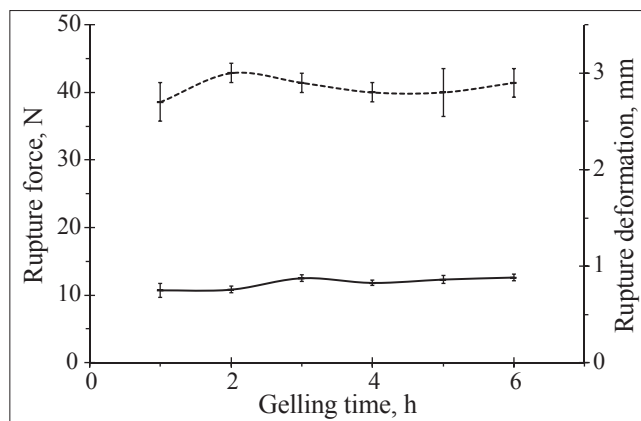
a) 30 g.kg^{-1} Na-alg., 40 g.kg^{-1} C$_6$H$_{10}$O$_6$Ca and 650 g.kg^{-1} sucrose

b) 60 g.kg^{-1} Na-alg., 40 g.kg^{-1} C$_6$H$_{10}$O$_6$Ca and 650 g.kg^{-1} sucrose

c) 30 g.kg^{-1} Na-alg., 70 g.kg^{-1} C$_6$H$_{10}$O$_6$Ca and 650 g.kg^{-1} sucrose

d) 60 g.kg^{-1} Na-alg., 70 g.kg^{-1} C$_6$H$_{10}$O$_6$Ca and 650 g.kg^{-1} sucrose

Fig. 4. Rupture force (——) and deformation (- - -) in function of gelling time for sodium alginate with calcium-lactate and sucrose

the 60 g.kg^{-1} Na-alg., 70 g.kg^{-1} C$_6$H$_{10}$O$_6$Ca and 650 g.kg^{-1} sucrose and the 60 g.kg^{-1} Na-alg. + 70 g.kg^{-1} C$_6$H$_{10}$O$_6$Ca combination (Fig. 3d and 4d) the difference was between 47.6 percent and 55.6 percent.

- The smallest decrease of the rupture force was observed with the combination of 30 g.kg^{-1} Na-alg., 70 g.kg^{-1} C$_6$H$_{10}$O$_6$Ca and 650 g.kg^{-1} sucrose (Figure 4c) versus 30 g.kg^{-1} Na-alg. + 70 g.kg^{-1} C$_6$H$_{10}$O$_6$Ca (Figure 3c) by 27.0% to 43.5%.

- It was also found that the reduction of maximum deformation is the smallest – 0.2 mm – between 60 g.kg^{-1} Na-alg., 70 g.kg^{-1} C$_6$H$_{10}$O$_6$Ca and 650 g.kg^{-1} sucrose (Figure 4d) versus 6% Na-alg. + 70 g.kg C$_6$H$_{10}$O$_6$Ca (Figure 3d). The largest reduction in deformation – from 0.2 to 0.7 mm – is the combination 30 g.kg^{-1} Na-alg., 40 g.kg^{-1} C$_6$H$_{10}$O$_6$Ca and 65 g.kg^{-1} sucrose (Figure 4a) versus 30 g.kg^{-1} Na-alg. +40 g.kg^{-1} C$_6$H$_{10}$O$_6$Ca (Figure 3a).

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