

# Gelation of Calcium Alginate. Influence of Rice Starch or Rice Flour on the Gelation Kinetics and on the Final Gel Structure

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Gelation of calcium alginate in the presence of rice starch or flour was studied. Rate constants, structural diffusion resistance constants, diffusion coefficients, and activation energies of gelation were determined from the gelation time curves. The heterogeneous structural resistance constants were independent of temperature but in the mixtures of calcium alginate with starch depended strongly on the quantity of starch. Activation energy of calcium alginate gelation was 4777 cal/mol. In the presence of rice starch or flour the heterogeneous structural resistance and the activation energy of gelation (9623 cal/mol) increased and the gelation rate decreased. The addition of rice starch or flour to calcium alginate resulted in coarser and more rigid gels with decreased elasticity and resistance to twist and shear. Some of these structural properties of the final gel, for example, the coarseness and rigidity, could be characterized by the kinetic constants of gelation. Because these changes were proportional to the amount of rice starch or flour added to the alginate, it was possible to regulate the viscoelastic properties of calcium alginate gels in this manner.

Alginates are copolymers of L-guluronic and D-mannuronic acids (Haug, 1959; Smidsrod and Haug, 1965; Smidrod, 1974) and for their gelation properties are used in many food products, especially in mixtures with other polysaccharides (Furia, 1972; McDowell, 1975). Calcium alginate gels are low-calorie foods (only 1.4 cal/g) and, when compared to other food gels, have many advantages, for example, quick setting time without a need for refrigeration. Their disadvantage is that they do not melt in the mouth, and thus, for obtaining satisfactory results, it is important to control their set rates and final structures.

To regulate the gelation properties of alginate mixtures, they were used in low concentrations or in the mixtures with weak acids, gel retarding agents, carboxymethyl alginates, and/or (carboxymethyl)cellulose (Furia, 1972; Littlecote, 1980; Challen et al., 1982; Eklund, 1987).

Numerous patents have been issued and papers published relating to the preparation of foods in the presence of alginate gels. Alginates have been used in dry milk puddings, as ice cream stabilizers, as preservative coatings for meat and fish, for fixation of flavor, in salad dressings, simulated fruit, sauces, relishes, puddings, jellies, and cakes, in freeze damage resistant foods, and in low-calorie foods (Furia, 1972; Unilever, 1974; Luh et al., 1976; Hsu, 1985; Eklund, 1987).

In this work the gelation of calcium alginate and that of mixtures of calcium alginate with rice starch and/or rice flour have been studied with different alginate gels at different temperatures.

## EXPERIMENTAL PROCEDURES

**Materials.** Sodium alginates (from *Macrocystis pyrifera*) and other chemicals were from Sigma Chemical Co., St. Louis, MO. Instead of molecular weights of the alginates, the manufacturer shows the viscosities of 2% solutions (in centipoise). Oryzenin and rice starch or flour were prepared from the same variety of polished rice (Mars, medium grain) as described by Chrastil (1990a-c).

**Gel Formation.** Sodium alginate (2% solution in H<sub>2</sub>O) or its mixture with starch [(20 g of alginate + 50 g of starch)/L of H<sub>2</sub>O] or flour [(20 g of alginate + 50 g of flour)/L of H<sub>2</sub>O] and/or starch plus oryzenin [(20 g of alginate + 45 g of starch + 5 g of oryzenin)/L of H<sub>2</sub>O] was cooked for 30 min in a boiling water

bath. All samples were from the same rice variety (Mars, medium grain), and the mixture of starch with oryzenin imitated approximately the composition of flour. The suspension was cooled to the gelation temperature (see tables) and carefully mixed in a 1-L beaker with 500 mL of 5% CaCl<sub>2</sub> of the same temperature.

The mixing was done by pouring the calcium salt solution on the wall of the slightly tilted beaker to avoid complete mixing of viscous alginate and calcium solution. The gel was formed quickly at the boundary between these two liquid layers. By a slow rotary movement of the beaker and by molding the gel with a pestle or other similar blunt-flat instrument almost perfect spheres were formed. A duplicate set of 10 equal spheres from the same solutions was prepared, and after selected time intervals, the outer solutions were decanted, the diameters of the spheres measured, and the spheres cut in half.

The extent of gelation was measured by the boundary between the viscous alginate in the center of the sphere and the rigid calcium alginate gel crust. Above 40% calcium saturation limit (determined by calcium analysis of the gels) calcium alginate gels were rigid, but below this limit they remained as viscous liquids.

## RESULTS AND DISCUSSION

From the studies of the calcium alginate gelation time curves it became apparent that these curves could be accurately expressed by the binomial diffusion equation derived and used for other diffusion-limited reaction systems (Chrastil, 1988a,b, 1989, 1990a,d)

$$L = L_{\max}[1 - \exp(-kt)]^n \quad (1)$$

where  $L$  is the length of gelation (thickness of the gel) at time,  $t$ ,  $L_{\max}$  is the gelation length at  $t \rightarrow \infty$  (gelation of the sphere is complete and thus equals the radius of the sphere),  $k$  is the gelation rate constant, and  $n$  is the heterogeneous structural resistance constant which is indirectly proportional to the resistance. All constants of eq 1 can be easily obtained graphically from the log-log plots of  $L$  vs  $t$  or calculated by a computer program from the time curves by using mathematical regression methods (Chrastil, 1988a,b).

Calcium alginate gels prepared by this method were spheres. Thus,  $L_{\max}$  in eq 1 was the radius of the sphere and  $L$  was the thickness of the gelled crust (length of ge-

Table I. Gelation of Calcium Alginate Gel<sup>a</sup>

time, h	alginate, 14 000 cps							
	alginate, 250 cps 25 °C L, %		5 °C L, %		25 °C L, %		50 °C L, %	
	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
2	8.9	8.9	6.1	6.1	9.2	9.3	11.7	11.7
4	16.6	16.6	10.3	10.3	16.0	15.9	19.6	19.7
6	23.4	23.4	14.0	14.0	21.5	21.5	26.3	26.3
8	29.1	29.7	16.8	16.8	26.3	26.4	31.5	31.9
24	63.5	63.8	37.9	37.1	54.5	54.3	62.9	62.9
32	74.0	73.9	44.8	44.7	63.4	63.5	72.3	72.2
48	86.1	86.4	57.4	57.0	76.6	76.5	83.9	84.2
72	95.2	94.9	70.2	70.2	87.6	87.7	92.9	92.9
96	98.0	98.1	78.9	79.0	93.5	93.5	96.9	97.0
120			85.2	85.1	96.5	96.5	98.6	98.6
$L_{max} = 100$			$L_{max} = 100$		$L_{max} = 100$		$L_{max} = 100$	
$n = 0.9457$			$n = 0.7813$		$n = 0.7957$		$n = 0.7836$	
$k = 0.0405$			$k = 0.0140$		$k = 0.0261$		$k = 0.0336$	
$r = 0.9997$			$r = 0.9999$		$r = 1.0000$		$r = 1.0000$	
$D = 6.1 \times 10^{-10}$			$D = 4.9 \times 10^{-9}$		$D = 9.2 \times 10^{-9}$		$D = 1.8 \times 10^{-8}$	

<sup>a</sup>  $L$ ,  $L_{max}$  is length of gelation in %,  $k$  is in  $h^{-1}$ ,  $D$  is in  $cm^2 s^{-1}$ , and  $r$  is the statistical correlation coefficient between the experimental and calculated values (eq 1).

Table II. Gelation of Calcium Alginate Gel Cooked with Rice Starch or Flour<sup>a</sup>

time, h	alginate + rice flour, 22 °C L, %		alginate + rice starch					
	exptl	calcd	5 °C L, %		22 °C L, %		50 °C L, %	
			exptl	calcd	exptl	calcd	exptl	calcd
2	9.8	9.8	15.4	15.3	23.8	23.6	44.7	46.2
4	13.4	13.4	20.8	20.9	32.5	32.1	59.2	59.7
6	16.1	16.1	25.0	25.0	38.8	38.2	62.4	68.5
8	18.8	18.2	28.5	28.3	42.5	43.1	75.0	74.8
24	30.0	29.5	45.0	45.2	66.2	66.0	94.7	94.6
32	33.8	33.4	50.8	50.8	72.5	72.6	97.4	97.4
48	40.0	39.7	59.3	59.3	81.2	81.7		
72	47.5	46.9	68.2	68.5	90.0	89.6		
96	52.5	52.6	75.0	75.1	93.8	93.9		
120	57.5	57.3	80.1	80.1	96.4	96.4		
$L_{max} = 100$			$L_{max} = 100$		$L_{max} = 100$		$L_{max} = 100$	
$n = 0.448$			$n = 0.451$		$n = 0.454$		$n = 0.422$	
$k = 0.00283$			$k = 0.00786$		$k = 0.0213$		$k = 0.08746$	
$r = 0.9999$			$r = 1.0000$		$r = 0.9998$		$r = 0.9997$	
$D = 4.7 \times 10^{-6}$			$D = 1.1 \times 10^{-5}$		$D = 2.5 \times 10^{-5}$		$D = 1.6 \times 10^{-4}$	

<sup>a</sup> Alginate (2%) had 14 000 cps.  $L$ ,  $L_{max}$  is length of gelation in %,  $k$  is in  $h^{-1}$ ,  $D$  is in  $cm^2 s^{-1}$ , and  $r$  is the statistical correlation coefficient between the experimental and calculated values (eq 1).

lation) which grew from the outer calcium solution into the sphere and formed a rigid calcium alginate gel. During gelation small shrinkage of the sphere caused by syneresis was observed, especially at higher temperatures. This shrinkage was smaller than 10% and was corrected automatically during the calculations because the length of gelation was expressed in relative percent of the radius.

With the same gelation mixture the structural diffusion resistance,  $n$ , did not depend on temperature (between 5 and 50 °C) and alginate concentration (between 2 and 3%; not shown here), but it did depend on the gel structure (Tables I and II). For example,  $n$  decreased with the molecular weight (expressed by manufacturer as viscosity) of the original alginate. It also decreased very significantly in the gels made from the mixtures of alginate with rice starch or flour.

The gelation kinetic constants,  $L_{max}$ ,  $n$ , and  $k$ , did not depend on the chemical structure of the calcium salts used for gelation. The results with  $CaCl_2$ , calcium acetate, calcium lactate, and calcium tartrate were not significantly different.

However, the gelation rate constant,  $k$ , depended on alginate or calcium concentration and alginate composition. For example, the composition of Kelgin HV from

*Ascophyllum nodosum* is different (molar fractions of guluronic acid and mannuronic acid were 0.36 and 0.64, respectively) from the composition of another alginate, Mannugel DMB from *Laminaria hyperborea* (molar fractions of guluronic acid and mannuronic acid were 0.68 and 0.32, respectively), and these two alginates had different rate constants,  $k$ , under the same conditions (temperature and concentrations).

The relationship between the rate constant,  $k$ , and the alginate or calcium concentration was almost linear (anyway, the use of alginate for calcium gelation is limited to a narrow range, 1–4%, because of very high viscosities of more concentrated solutions). The relationship between the rate constant,  $k$ , and the alginate chemical composition was more complex and is not shown here. Nevertheless, the kinetic behavior of different alginates could always be accurately expressed by eq 1.

The rate constants,  $k$ , increased with temperature by Arrhenius equation:  $k = \exp(-\Delta E^*/RT + b)$ , where  $\Delta E^*$  was an activation energy of calcium alginate gelation.

By comparison with Fick's integrated diffusion series for spheres (Crank, 1956) at short reaction times we got

the diffusion coefficients (Chrastil, 1989, 1990d):

$$D = \pi(k)^{2n}(L_{\max})^2/36 \quad (2)$$

The gelation with low molecular weight (low viscosity) alginates was almost a first-order reaction [the heterogeneous structural resistance constant,  $n$ , was almost 1 (0.946 with 250 cps 2% sodium alginate)] but the resistance increased (constant,  $n$ , decreases with increased resistance) with the higher molecular weight (higher viscosity) alginates (for example,  $n$  was 0.8 with 14 000 cps alginate). The rate constants,  $k$ , decreased with the molecular weight of alginate (0.040 and 0.026 with 250 and 14 000 cps alginates, respectively). The activation energy of gelation with 14 000 cps alginate was 4738 cal/mol. The diffusion coefficient,  $D$ , increased with gelation temperature and decreased with molecular weight (viscosity) of alginate (Table I).

The addition of rice starch to the alginate increased the heterogeneous structural resistance (constant,  $n$ , decreased from 0.8 to 0.45), decreased the rate constant,  $k$ , and increased the diffusion coefficient,  $D$ , in the cooked alginate-starch mixtures (Tables I and II). The activation energy of alginate gelation in the presence of rice starch almost doubled (9623 cal/mol) when compared to that of alginate alone. Starch probably interacted with alginate by blocking the free carboxyl groups of alginate with additional hydrogen bonds between these two polysaccharides. Because during gelation these bonds must be broken and replaced by calcium, such an inhibition of carboxyl groups would increase the activation energy of gelation.

The addition of oryzenin (rice storage protein) to the rice starch-alginate mixtures resulted in smaller rate constants,  $k$ . Similar decrease of the rate constants,  $k$ , was obtained with alginate-rice flour mixtures (rice flour contained almost 10% oryzenin) (Table II). This was probably caused by protein-starch and/or protein-alginate binding in the cooked alginate-rice flour mixtures because the binding of oryzenin to starch in rice changes its physicochemical properties and increases the stickiness of starch (Chrastil, 1990b,c).

The final calcium alginate gel structures obtained with different alginates (250, 3500, and 14 000 cps) were not much different from each other. Fine, soft, and elastic gel structures resulted from these alginates.

On the other hand, in the presence of rice starch and/or rice flour, coarser and more rigid gel structures were obtained. The coarsening was reflected by an increased diffusion coefficient,  $D$ , and the rigidity by decreased kinetic constants,  $n$  and  $k$ . When compared with the pure calcium alginate gels, the gels to which rice starch or flour was added had decreased elasticity and resistance of the

gel to twist and shear. On the other hand, the hardness increased. The extent of these changes was proportional to the amount of starch or flour in the gel. Thus, the viscoelastic properties of the calcium alginate gels can be regulated by the addition of rice starch or flour.

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