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EVALUATION OF STRESS-STRAIN FOR CHARACTERIZATION OF THE RHEOLOGICAL BEHAVIOR OF ALGINATE AND CARRAGEENAN GELS

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Abstract - The stress-strain of samples deformed until failure and the relaxation response after 50% deformation of the initial height under constant stress were obtained. Uniaxial compression and stress-relaxation tests enabled satisfactory differentiation of the mechanical resistance of gels with different alginate and carrageenan concentrations. Higher values for initial force at the beginning of the relaxation test were associated with higher calcium uptake by the gels. An increment of failure stress during the uniaxial compression tests for higher concentration of calcium in the gel structure was also observed. The maximum amount of cation uptake was higher than the theoretical value for saturation of all the carboxylic groups available in alginate molecules due to structural rearrangements. Stress-relaxation tests indicated that the residual stress of the gel increased with κ-carrageenan concentration.

Keywords: alginate-carrageenan gel, compression-relaxation tests, rheology.

INTRODUCTION

In the food industry, alginates and carrageenans are used for their gelling properties. In many applications, foods are mixed with gelling agents, approved by food regulations, for thickening and improving rigidity and texture stability (Glicksman, 1983). These polysaccharides may also be used to immobilize enzymes for carrying out important bioprocesses (Bales, 1994). Consequently, chemical and mechanical behaviors must be studied to enable selection of the appropriate catalyst for a reaction system.

In this case, gel formation occurs by molecule aggregation in the presence of effective cations. This quite complex operation depends on the type of polymer, the degree of polymerization and methods of preparation (Mancini et al., 1999). Therefore, gel strength differs according to structure. The mechanical resistance measured by rheological tests is indicative of gel strength (Nussinovitch et al., 1989). The uniaxial compression test and the stress-relaxation response curves are related to the cross-linking of polymer chains, which depends on product composition and gelling conditions. The objective of this work was to study the gels behavior using uniaxial compression and stress-relaxation tests for samples with different κ-carrageenan and sodium alginate concentrations and gelling conditions.

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THEORY

A number of materials show time dependence in their elastic response, referred to as viscoelasticity, which is typical of polymeric materials. Stress-relaxation tests are commonly used to study this phenomenon. When a polymeric liquid or solid is compressed and allowed to relax, the stress decays in an exponential fashion.

The stress-relaxation curves for gels have traditionally been described in terms of a discrete linear-Maxwell model (Mitchell, 1976). Since gels are not physically stable and tend to exchange moisture with the environment, tests for long-term determination of their relaxation pattern (t > 20 min) are difficult to perform. Consequently, the relaxation parameters were determined in experiments of short duration using a mathematical model suggested by Peleg (1979, 1980) to characterize the relaxation behavior of polysaccharide gels.

The relaxation curve can be represented by

$$\frac{F_{(t)}}{F_0} = 1 - \frac{t}{a + b\,t} \tag{1}$$

or in linearized form

$$\frac{F_0\,t}{F_0 - F_{(t)}} = a + b\,t \tag{2}$$

where F_0 is the initial force at the beginning of the relaxation test, $F_{(t)}$ is the decaying force, and a and b are constants. The linear dependence of stress relaxation on strain is called linear viscoelasticity.

Constant a represents the amount of stress that remains unrelaxed. If a = 0, all the stress relaxes and the material is considered to be a purely viscous liquid. If a > 0, there is a residual stress even when $t \to \infty$ and the material is considered to be a viscoelastic liquid or solid. The magnitude of a can be used to measure solidity (for a viscoelastic liquid the stress relaxes to zero, while for a viscoelastic solid it asymptotically approaches an equilibrium stress). However, for nonlinear viscoelastic materials, the magnitude of a may depend on the deformation history of the specimen, and consequently, the specimen can exhibit different degrees of solidity for different strains. Constant b represents the rate at which the stress relaxes. If b = 0, the stress does not relax (e.g., an ideal elastic solid) (Peleg, 1980).

A hypothetical asymptotic modulus, E_A, can be calculated from

$$E_A = \frac{F_0}{A_{(t)}\ \varepsilon}\left(1 - \frac{1}{b}\right) \tag{3}$$

where $A_{(t)}$ is the specimen's cross-sectional area and ε is the strain. In materials with linear viscoelastic behavior, E_A should be independent of strain and strain history. In materials with nonlinear behavior, E_A may indicate whether the deformation involves internal fracture, compressibility or strain hardening and can be used to predict failure.

The force data from the testing machine were converted to apparent stress, $\sigma_{a(t)}$, and to true stress, $\sigma_{(t)}$, according to the following definitions (Rosenau et al., 1978)

$$\sigma_{a(t)} = \frac{F_{(t)}}{A_0} \tag{4}$$

$$\sigma_{(t)} = \frac{F_{(t)}\left(H_0 - \Delta H_{(t)}\right)}{A_0\,H_0} \tag{5}$$

where H_0 is the initial specimen length, $\Delta H_{(t)}$ the actual absolute deformation that is determined during the test and A_0 the cross-sectional area of the original specimen.

The time data from the testing machine were converted to Hencky's strain, $\varepsilon_{H(t)}$

$$\varepsilon_{H_{(t)}} = \ln\left(\frac{H_0}{H_0 - \Delta H_{(t)}}\right) \tag{6}$$

The slope of the linear portion of the stress-strain relation was defined as the deformability modulus, E_D

$$E_D = \frac{\sigma_{(t)}}{\varepsilon_{H_{(t)}}} \tag{7}$$

E_D has stress units and can be used as a measure of gel stiffness.

MATERIALS AND METHODS

Sample Preparation

Food-grade commercial alginates Kelgin L.V. (low viscosity) and Kelgin H.V. (high viscosity) from Kelco Division of Merck & Co (Chicago, USA) and κ-carrageenan Gelacid C-3 from Biotec S.A. (Buenos Aires, Argentina) were used for gel preparation. $CaCl_2$ and KCl of analytical quality were from Mallinckrodt (St. Louis, USA).

Gel cylinders with a 1.1-cm diameter and a 2.0-cm length were prepared as described by Mammarella and Rubiolo (1997). The range of gel compositions and gelling conditions used in the tests were determined according to previous work (Mammarella, 2001).

Sample Identification

A code composed of letters and numbers was assigned for sample identification. A key letter was used to identify the composition of the substance followed by a number of which each digit corresponds to a level of concentration of the gel or composition of the solution according to the following code:

G: gel composition.

First number: high viscosity sodium alginate; 1, 2, and 3 are 1.0%, 2.0%, and 3.0%, respectively.

Second number: low viscosity sodium alginate; 0 and 1 are 0.0% and 1.0%, respectively.

Third number: κ-carrageenan; 0, 1, 2, 3, and 4 are 0.0%, 0.1%, 0.5%, 1.0%, and 2.0%, respectively.

K: composition of immersion solution.

First number: $CaCl_2$; 1, 2, and 3 are 1.0%, 2.0%, and 3.0%, respectively.

Second number: KCl; 0 and 1 are 0.0% and a concentration two times the $CaCl_2$ concentration, respectively.

Finally, the letter T represents the time that gels remained in the immersion solution, while the number that follows is the time level. Levels 1, 2, 3, 4, 5, and 6 correspond to 0.5 h, 1.0 h, 1.5 h, 2.0 h, 2.5 h, and 3.0 h, respectively.

Example: the sample identified as G100-K11-T6 is a gel of 1.0% high viscosity sodium alginate without addition of low viscosity sodium alginate or κ-carrageenan, placed in $CaCl_2$ (1.0%) and KCl (2.0%) immersion solution during 3.0 h.

Mechanical Tests

A Shimadzu universal testing machine, model DSS-10TS with a 50 N max load compression cell was used. Gel specimens were compressed to 50% deformation before relaxation for approximately 8-9 min (Peleg 1979). The deformation rate was 10.0 mm min^{-1} and triplicate tests were performed in all cases. Compression-relaxation data were recorded and analyzed using a computational program developed in Visual Basic language. Failure stress was measured by compression until gel fracture was detected.

RESULTS AND DISCUSSION

The stress-relaxation data were modeled using Eq. (2) to obtain the rheological parameters of Eqs. (3) to (7) (Table 1). The higher values of F_0 may be associated with higher level of calcium incorporation into gels (Figure 1). The hydrocolloid molecules are close to each other due to the interactions with the cations and the bridge of hydrogen bonds that improve gel hardness. The calcium uptake depends on the gelling conditions, such as Ca^{2+} concentration of the immersion solution (Figure 1.a), immersion time (Figure 1.b), or alginate concentration in the gel (Figure 1.c). Moreover, an increment of failure stress during the uniaxial compression test for higher concentrations of calcium in the gel structure was also observed. The failure stress values for gels G200-K20-T6 and G203-K21-T6 were 182.5 kPa and 116.7 kPa, respectively.

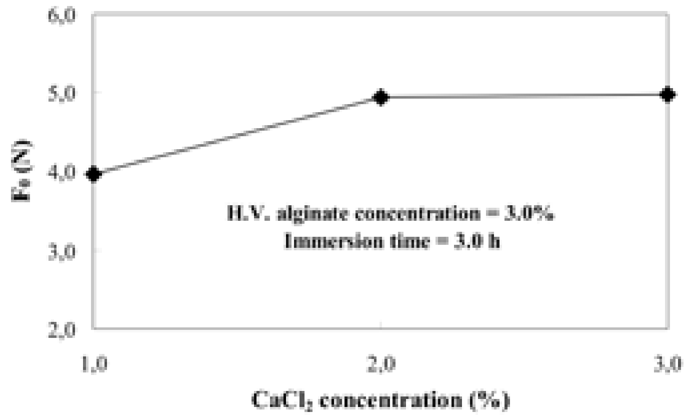
Stress-relaxation tests indicated that the residual apparent stress of the gel increased with κ-carrageenan concentration due to the fact that this component forms a more elastic gel (Figure 2) (Glicksman, 1983). Furthermore, a lower residual apparent stress was observed for the gel when L.V. alginate was used to obtain the same total alginate concentration (Figure 3).

Important differences in parameter a were observed for the gels studied. However, different values for parameter b were only found when κ-carrageenan was added.

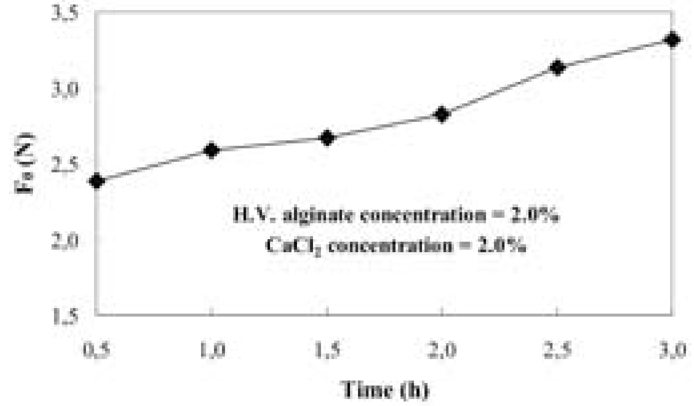
The changes in a can be analyzed through E_D because both parameters are a measurement of gel rigidity. Values of E_D changing with Ca^{2+} concentration of the immersion solution, immersion time, and H.V. alginate concentration followed the same trend as F_0, as expected. Figure 4 shows that E_D values change with $CaCl_2$ concentration for different H.V. alginate concentrations. The E_D values increased until reaching a critical Ca^{2+} level for each H.V. alginate concentration, which is related to stoichiometry (Mancini et al., 1999). However, that maximum amount of cation uptake can be higher (approximately 3-5% higher than the stoichiometry) due to structural rearrangements that allow the uptaking of more calcium cations.

Parameter b increased for higher κ-carrageenan concentrations, indicating that the gel residual stress also increased (Table 1). Parameter b can be related to E_A analysis. However, because E_A values depend on deformation history, gel behavior following the addition of κ-carrageenan can not be predicted.

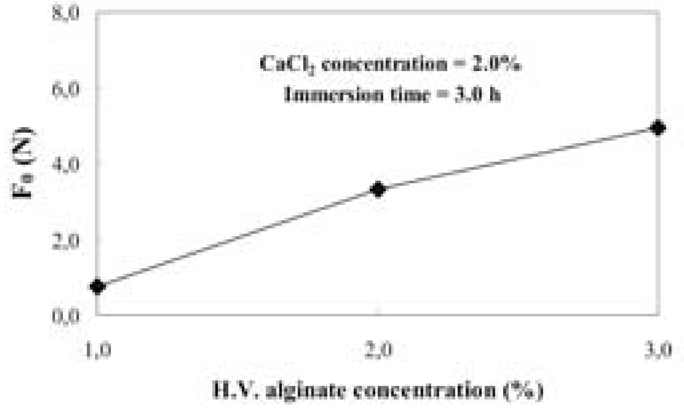
These results provide a general guideline for formulating hydrocolloid gels with a broad range of textural properties. Brittle gels of varied stiffness values can be obtained at different alginate concentrations using calcium ion concentrations above the critical ion level. Extensible gels of a desired stiffness can be obtained at a given alginate concentration with relatively low calcium ion concentrations.



(a)



(b)



(c)

Figure 1: Effect of calcium uptake by the gel on the initial force at the beginning of the relaxation test, F_0, for gels without L.V. sodium alginate and κ-carrageenan and no KCl in the immersion solution.

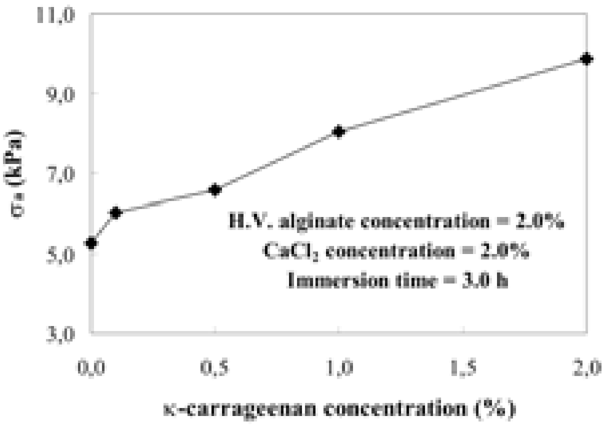


Figure 2: Effect of κ-carrageenan on the residual apparent stress of the gel, $\sigma_{a_{(t\to\infty)}}$.

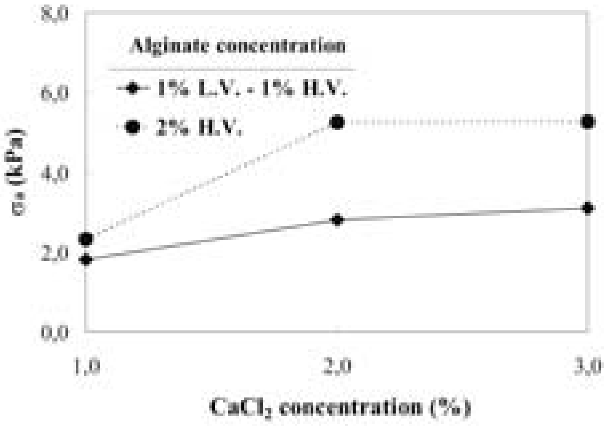


Figure 3: Effect of the H.V.:L.V. alginate ratio on the residual apparent stress of the gel, $\sigma_{a_{(t\to\infty)}}$, for 3.0 h of immersion time.

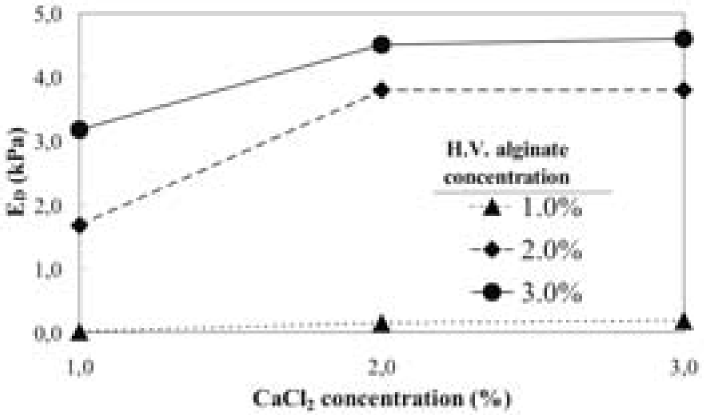


Figure 4: Effect of calcium uptake by the gel on the strength deformability modulus, E_D, for gels without L.V. sodium alginate, κ-carrageenan, no KCl in the immersion solution, and 3.0 h of immersion time.

Table 1: Relaxation parameters of gel specimens compressed to 50% deformation and allowed to relax for approximately 8-9 min.

Specimen	F_0 (N)	$\sigma_{a(t\to\infty)}$ (kPa)	$\sigma_{(t\to\infty)}$ (kPa)	E_A (kPa)	E_D (kPa)	Linearized relaxation parameters		
						a	b	R^2
G100-K10-T6	0.535	0.021	0.010	0.000	0.015	0.02	1.00	1.000
G100-K20-T6	0.759	0.209	0.104	0.157	0.151	0.18	1.01	0.999
G100-K30-T6	0.795	0.251	0.125	0.326	0.181	0.15	1.02	0.999
G110-K10-T6	3.245	1.807	0.904	0.671	1.304	0.22	1.01	1.000
G110-K20-T6	3.312	2.810	1.405	0.000	2.027	0.15	1.00	1.000
G110-K30-T6	3.323	3.092	1.546	0.687	2.231	0.17	1.01	1.000
G200-K10-T6	3.313	2.319	1.160	2.016	1.673	0.31	1.03	0.999
G200-K20-T1	2.386	2.142	1.071	3.261	1.545	0.39	1.07	0.999
G200-K20-T2	2.588	2.904	1.452	0.556	2.095	0.17	1.01	1.000
G200-K20-T3	2.667	3.050	1.525	0.000	2.200	0.17	1.00	1.000
G200-K20-T4	2.826	3.886	1.943	0.000	2.803	0.16	1.00	1.000
G200-K20-T5	3.133	4.826	2.413	0.731	3.481	0.26	1.01	1.000
G200-K20-T6	3.317	5.255	2.627	0.686	3.790	0.18	1.01	1.000
G200-K30-T6	3.543	5.265	2.633	0.000	3.798	0.17	1.00	1.000
G201-K11-T6	3.364	4.168	2.084	8.631	3.007	0.47	1.14	0.999
G201-K21-T6	3.908	5.975	2.988	5.342	4.310	0.51	1.07	0.990
G201-K31-T6	3.974	6.038	3.019	6.150	4.356	0.49	1.08	0.999
G202-K11-T6	3.691	4.659	2.330	3.672	3.361	0.50	1.05	0.999
G202-K21-T6	4.297	6.268	3.134	5.873	4.521	0.48	1.07	0.999
G202-K31-T6	4.372	6.571	3.285	1.791	4.740	0.35	1.02	0.999
G203-K11-T6	3.983	5.192	2.596	8.916	3.745	0.58	1.12	0.999
G203-K21-T6	4.429	7.616	3.808	5.238	5.493	0.48	1.06	0.999
G203-K31-T6	4.427	8.033	4.017	4.404	5.795	0.43	1.05	0.999
G204-K11-T6	4.215	6.560	3.280	7.271	4.732	0.69	1.09	0.998
G204-K21-T6	6.220	9.548	4.774	7.356	6.888	0.43	1.06	0.999
G204-K31-T6	6.221	9.872	4.936	7.357	7.121	0.47	1.06	0.999
G300-K10-T6	3.954	4.398	2.199	5.404	3.172	0.40	1.07	0.999
G300-K20-T6	4.939	6.247	3.124	1.022	4.506	0.19	1.01	0.999
G300-K30-T6	4.976	6.383	3.191	1.029	4.604	0.14	1.01	1.000

CONCLUSIONS

Uniaxial compression and stress-relaxation tests can be used to determine the change in mechanical resistance with alginate and carrageenan gel concentrations.

Higher stiffness values were found in gels with higher alginate and calcium concentrations. The maximum amount of cation uptake was slightly higher than the value necessary to theoretically saturate all the available carboxylic groups in each alginate molecule present.

Stress-relaxation tests indicated that the residual stress of the gel increased with κ-carrageenan concentration.

The rheological behavior of the gels was described by relationships similar to those in the models for viscoelastic solids.

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