Effect of two kinds of cryoprotectants in the viscoelasticity of squid surimi gels during frozen storage

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ABSTRACT

Influence of two kinds of cryoprotectants (sorbitol + sucrose and sorbitol + trehalose) on the viscoelastic properties of squid (*Dosidicus Gigas*) surimi gels during six months of frozen storage was studied. Rheological measurements showed that sorbitol + sucrose preserve better the gel structure than sorbitol + sucrose.

INTRODUCTION

Surimi production is aimed toward concentrating myofibrillar proteins by removing sarcoplasmatic proteins through continuous washing of the muscle mince[1]. Gelation ability is an important indication of functional and textural properties of surimi[2] in order to the elaboration of new derivative products.

During frozen storage, the unfolding of myofibrillar proteins (mainly myosin) exposes nonpolar amino acids which become available for formation of hydrophobic interactions with like groups in the vicinity. This process leads to protein aggregation, textural changes and loss of gelling and water-holding functionality[3]. The addition of cryoprotectans is required in order to retain the surimi fuctional properties. There are a lot of compounds like some low molecular weight sugars and polyols as well as many aminoacid, carboxylic acids and polyphosphates that were found to be cryoprotective[4]. The primary cryoprotectant in the manufacture of surimi is sucrose and sorbitol alone or mixed because of their relative low cost and good availability. Trehalose is a non-reducing disaccharide with low caloric value and sweetness, only 45% of that sucrose, for that reason is a good new alternative cryoprotectant in surimi industry.

The aim of this work is the evaluation of the influence of two kinds of cryoprotectans on the viscoelastic properties of squid surimi gels (Dosidicus Gigas) during the frozen storage, from an initial time (t_0) until six months later (t_1).

MATERIALS AND METHODS

The gel samples with 4% sucrose + 4% sorbitol were designated *GB2*, whereas their 4% sorbitol + 4% trehalose counterparts were named *GB3*.

Oscillatory (stress sweep and frequency sweep) and steady (creep and recovery) tests at 10ºC were programmed. All Rheological measurements were carried out using a Bohlin CVO controlled stress rheometer, Inc. (Bohlin Instruments Cranbury, NJ) and a Haake RS600 CD rheometer from Thermo Electron GmbH (Karlsruhe, Germany) [5].

The *stress sweep* data were used for knowing the linear viscoelastic range limit. Stress (σ) from low (10 Pa) to high σ (3500 Pa) were programmed. The frequency was 1Hz and a maximum shear strain of 100% was applied.

From *frequency sweep* test it can be obtained the mechanical spectra, and the fractal dimension values were calculated after the *G** power law fit. The range of frequency programmed was from 10 to 0,1 Hz under a constant shear strain (0,5%).

The *gel strength* values were obtained from *transient* tests. An instantaneous stress (within the linear viscoelastic region) during 600 s was applied in the creep test for each sample. When the stress was released, some recovery can be observed during other 600 s as the material attempts a return to the original shape[6].

RESULTS

Stress sweep test

This test allowed to determine the linear viscoelastic interval. Starting from these maximum amplitudes in terms of shear stress ($\sigma_{máx}$) and shear strain ($\gamma_{máx}$), it could be possible obtain the shear modulus (*G*) values (Table1).

For samples *GB3* the frozen storage time decreased considerably the shear modulus (*G*) values, so it can be said that the sample with sorbitol and trehalose experimented a considerable loss of rigidity.

Table 1. Shear modulus values samples *GB2* and *GB3* at 10ºC.

	(G ± S.D.)·10^{-4} (Pa)
***GB2* (t_0)**	4,034 ± 0,002
***GB3* (t_0)**	3,773 ± 0,014
***GB2* (t_1)**	3,922 ± 0,001
***GB3* (t_1)**	3,070 ± 0,013

On the other hand, the sample with sorbitol and sucrose didn't show any important changes in the consistency.

Considering the initial time, samples *GB2* show more rigid structure than *GB3* ones. This behaviour is kept along the six months of frozen storage.

Frequency sweep test

Figure 1 shows the evolution of the complex modulus (*G**) for samples *GB2* and *GB3* during frozen storage.

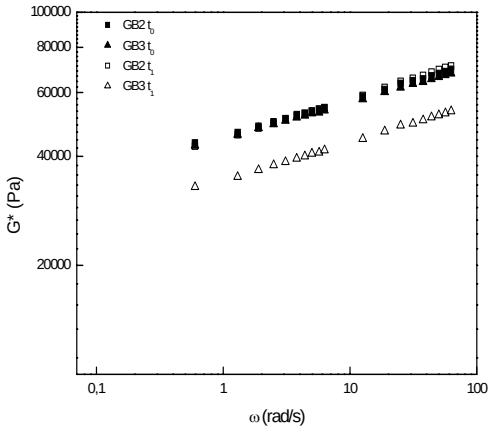

Figure 1. Mechanical spectra from frequency sweep test data. Samples *GB2* and *GB3* at 10ºC.

The *G** values for samples with sorbitol and trehalose decrease significantly along the six months, showing a less structural hardness according to the stress sweep test. Conversely, samples with sorbitol and sucrose don't present meaningful variations.

After the *G'* and *G''* power law fit (Eq. 1 and 2):

$$G' = G_0' \cdot \nu^{n'} \quad (1)$$

$$G'' = G_0'' \cdot \nu^{n''} \quad (2)$$

For samples *GB2* there is no variety in the viscoelastic moduli with the storage time (Table 2) and the structure remains practically unalterable, only n' and *n''* increase slightly showing a little loss of temporal stability (Table 3).

Table 2. Storage and loss moduli values from Eq. 1 and 2, samples *GB2* and *GB3* at 10ºC.

	GB2	***GB3***
$(G_0' \pm S.D.)\cdot 10^{-4}$ $(Pa\cdot s^n)$ (t_0)	5,392 ± 0,002	5,307 ± 0,0015
$(G_0'' \pm S.D.)\cdot 10^{-4}$ $(Pa\cdot s^n)$ (t_0)	0,9336 ± 0,0018	0,8877 ± 0,0018
$(G_0' \pm S.D.)\cdot 10^{-4}$ $(Pa\cdot s^n)$ (t_1)	5,387 ± 0,002	4,1046 ± 0,0013
$(G_0'' \pm S.D.)\cdot 10^{-4}$ $(Pa\cdot s^n)$ (t_1)	0,995 ± 0,002	0,7190 ± 0,0013

Table 3. *n'* and *n''* values from Eq. 1 and 2, for samples *GB2* and *GB3* at 10ºC.

	GB2	***GB3***
n' ± *S.D.* (t_0)	0,1021 ± 0,0006	0,0999 ± 0,0004
n'' ± *S.D.* (t_0)	0,102 ± 0,003	0,103 ± 0,003
n' ± *S.D.* (t_1)	0,1122 ± 0,0007	0,1060 ± 0,0005
n'' ± *S.D* (t_1).	0,115 ± 0,003	0,108 ± 0,003

On the other hand, samples with sorbitol and trehalose present a decrease of structural hardness. For that reason, we can say that sorbitol and sucrose preserve the viscoelastic properties of samples better than sorbitol and trehalose.

Creep and recovery

As it can be seen in Figure 2, it is possible to stand out the fact that for samples with sorbitol and trehalose the *J(t)* values experiment an increase in creep compliance values. However, samples with sucrose and sorbitol hardly change the *J(t)* values.

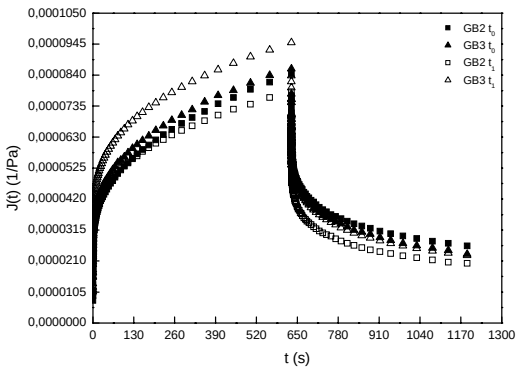

Figure 2. Comparison between compliance values as a function of time, at 10ºC.

The creep compliance data values allowed us to obtain the parameters *S* (gel strength) and *n* (relaxation exponent)[7] starting from the equation 3:

$$G(t) = S\cdot t^{-n} \qquad (3)$$

In Table 4, the *gel strength* values are shown for both samples.

Table 4. Gel strength and relaxation exponent values from eq.3 fit, samples *GB2* and *GB3*, at 10ºC.

	$(S \pm S.D.)\cdot 10^{-4}$ $Pa.\ s^n$	$n \pm S.D.$
GB2 (t_0)	3,740 ± 0,0014	0,153 ± 0,003
GB3 (t_0)	3,336 ± 0,011	0,142 ± 0,002
GB2 (t_1)	3,495 ± 0,009	0,138 ± 0,002
GB3 (t_1)	2,777 ± 0,007	0,134 ± 0,002

It is worth mentioning that for *GB3* samples there is a notable decreasing in the strength according to mechanical spectra data. Conversely, the variation for samples *GB2* is no meaningful.

S parameters allow us to affirm that sorbitol and sucrose origin a more strong gel than sorbitol and trehalose, this fact is kept during the frozen time according to oscillatory data.

CONCLUSIONS

Based on oscillatory test, we can say that samples with sorbitol and sucrose didn't experiment meaningful changes in the viscoelastic magnitudes. However, samples with sorbitol and trehalose presented a decrease in the consistency and hardness during the six months of frozen storage. The transient test corroborated the gel strength loss for samples with sorbitol and trehalose. Moreover, samples elaborated with sorbitol and sucrose generate a better gel than sorbitol and trehalose regardless the frozen time.

We can conclude that sorbitol and sucrose preserve better the functional properties of surimi gels along the storage.

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