Influence of the kind of cryoprotectant on the viscoelastic properties of squid surimi

Laura Campo and Clara A. Tovar

Dept. Applied Physics, University of Vigo, Facultad de Ciencias, As Lagoas, 32004 Ourense; campolau@gmail.com

ABSTRACT

The viscoelasticity of two squid surimis (*Dosidicus Gigas*), in raw and gel stage, elaborated with different kinds of cryoprotectant: B1 (4%sucrose + 4% sorbitol) and B2 (8% trehalose), was study. Oscillatory and transient test showed that B1 and B2 developed similar final gel structure.

INTRODUCTION

Surimi is the stabilized myofibrillar proteins obtained from mechanically deboned fish flesh that is washed with water, mixed with cryoprotectants and then frozen[1]. A new alternative for processing surimi is the use of cephalopod muscle given that the muscle is white, has little flavour and virtually no fat and is in abundant supply through the world[2].

Protein denaturation has been defined to describe a complex phenomenon involving alterations of the secondary and tertiary structure of proteins due to the breakage of the bonds that contribute to the stability of the native protein conformation without rupture of the covalent linkages between carbon atoms in the polypeptide chains. The cryoprotectants are used to avoid this process of denaturation[3].

The most commonly used cryoprotectant in the surimi industry is the 1:1 mixture of sucrose and sorbitol at a concentration of 8%, because of their relative low cost and good availability. The trehalose is another typical cryoprotectant which is very stable in properties and it can protect biological cells under adverse circumstances[4].

The aim of this work is the study of the influence of these two kinds of cryoprotectants on the viscoelastic properties of squid surimi (*Dosidicus Gigas*) as a function of its rheological quality.

MATERIALS AND METHODS

The samples with 4% sucrose + 4% sorbitol in raw and gel stage were designated *RB1* and *GB1*, respectively, whereas their 8% trehalose counterparts were named *RB2* and *GB2*.

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 (4000 Pa raw and 3500 gel samples) 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 temperature sweep tests were programmed at 0,1 Hz, under a constant shear strain (0,5%) and heating rate of 1ºC/min from 10 to 90ºC.

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

The limit of the lineal viscoelastic range is determined in terms of shear stress and shear strain. As it can be seen in Table 1, for *RB1* and *RB2* samples there are no significantly differences in stress and strain limit values.

Table 1. Stress and strain limit values for samples *B1* and *B2* at 10ºC.

	$\sigma_{máx}$ (Pa)	% $\gamma_{máx}$ ± S.D.
RB1	270	0,93 ± 0,36
RB2	256	1,26 ± 0,42
GB1	1270	3,16 ± 0,36
GB2	617	1,38 ± 0,29

Conversely, in samples *GB1* and *GB2* the differences are more evident. The limit stress value is bigger in sample *GB1* than in *GB2*, and the limit strain value is remarkably larger in *GB1* than in *GB2*, showing a more consistent and strong gel structure[7].

Frequency and temperature sweep tests

As it can be seen in Figure 1, the complex modulus (*G**) presents higher values in samples *RB1* than in samples *RB2*. These differences are smaller between gel samples.

For that reason, we can say that 4%sucrose + 4% sorbitol generates a more firm and consistent structure in raw samples than trehalose, but its gelation capacity is similar in both samples as can be seen in thermal rheogram that describes its profile gelation (Figure 2a, 2b).

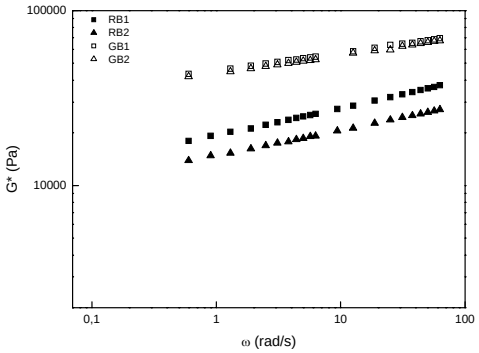
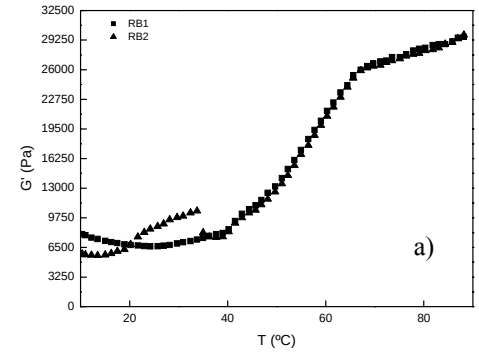


Figure 1. Complex modulus as a function of angular frequency, samples *B1* and *B2* at 10ºC.



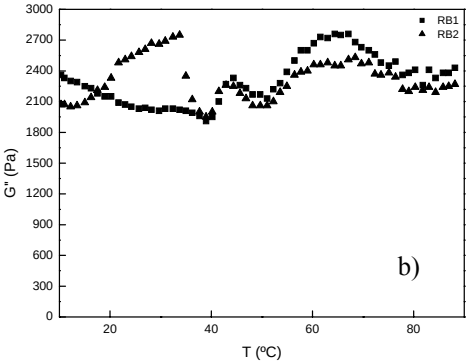


Figure 2. Temperature sweep test data. a) Storage moduli as a function of temperature, b) evolution of loss modulus with temperature, samples *B1* and *B2*.

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

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

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

It is possible to say that the influence of the cryoprotectant on the rheology of the raw stage is noticeable. As we can see in Table 2, the viscoelastic moduli are quite bigger in sample *RB1* than in *RB2* as we can see in Figure 1, with higher *n'* values than *RB2*, this fact allows us to affirm that this sample has got more hard structure and a less orderly initial network; perhaps due to samples with sorbitol and sucrose presents more content of denatured protein.

Table 2. Viscoelastic moduli values from Eq. 1 and 2, for raw samples at 10ºC.

	RB1	***RB2***
(G_0' ±*S.D.*)·10^{-4} (*Pa·s^n*)	2,481 ± 0,001	1,872 ± 0,0006
(G_0''±*S.D.*)·10^{-4} (*Pa·s^n*)	0,6962 ± 0,0010	0,4856 ± 0,001
n' ± *S.D.*	0,1570 ± 0,0007	0,1444 ± 0,0006
n'' ± *S.D.*	0,168 ± 0,003	0,165 ± 0,004

Table 3. Viscoelastic moduli values from Eq. 1 and 2, for gel samples at 10ºC.

	GB1	***GB2***
(G_0' ±*S.D.*)·10^{-4} (*Pa·s^n*)	5,392 ± 0,002	5,197 ± 0,004
(G_0''±*S.D.*)·10^{-4} (*Pa·s^n*)	0,934 ± 0,002	0,914 ± 0,0201
n' ± *S.D.*	0,1021 ± 0,0006	0,1040 ± 0,0011
n'' ± *S.D*	0,102 ± 0,003	0,105 ± 0,004

For gel samples, the oscillatory experiments provided similar viscoelastic moduli for both samples (Table 3), and similar structural order as it can be observed in the lower and analogues *n'* and *n''* parameters.

Creep and recovery

From creep and recovery data it can be obtain the compliance *J(t)*. Figure 3 shows that both samples *GB1* and *GB2* present similar values of *J(t).*

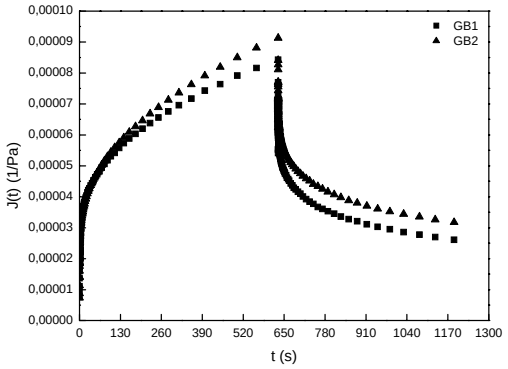


Figure 3. Compliance as a function of time, samples *GB1* and *GB2* at 10ºC

The creep compliance data values allowed us to obtain the parameters *S* (gel strength) and *n* (relaxation exponent)[8] starting from the equation 3:

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

As we can see in Table 4, the similitude between *GB1* and *GB2* samples given by frequency sweep data was corroborated by the similar *S* and *n* values.

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

	(S ± *D.E.*)·10^{-4} Pa. s^n	**n ± *S.D.***
GB1	3,740 ± 0,010	0,153 ± 0,003
GB2	3,863 ± 0,018	0,166 ± 0,003

CONCLUSIONS

By oscillatory and transient tests, we can affirm that for raw samples the trehalose favour the native protein structure more than sorbitol and sucrose.

On the other hand, considering the gelation profile the final gel structure is completely similar for both kinds of cryoprotectants.

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