Rheological evaluation of different stages of squid surimi made by two methods

Laura Campo and Clara A. Tovar

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

ABSTRACT

The viscoelastic properties in different physical stages: raw, suwari and gel of squid surimi (*Dosidicus Gigas*) elaborated by two methods were studied. So, viscoelastic moduli and fractal dimension from *stress and frequency sweep tests* showed that method *B* presents more native protein and developed better gel conformation than *A*.

INTRODUCTION

Proteins of fish muscle are normally used for processing a protein concentration (surimi). However, the cephalopod muscle has the potential to be used for manufacture of surimi being the intermediate material for surimi-based products. These products are based on the gel formation capacity of myofibillar proteins, given that the muscle is white, has little flavour and virtually no fat and is in abundant supply throughout the world[1].

For the surimi elaboration, the traditional method used in the washing for preparation fish surimi is very easy if the concentrate hasn't got a large number of enzymes and low molecular weight substances that give off bad odors. However, because of the easy solubility of muscular proteins in squid muscle, this method should be modified changing the typical washing by an acid washing at pH 5. For that reason, a new procedure based on isoelectric protein precipitation was designed.

The aim of this work is the study of the viscoelastic properties in different stages: raw, suwari and gel of squid surimi elaborated by these two methods.

MATERIALS AND METHODS

Samples from method *A* were made by initial dispersion of muscle in a neutral salt solution and further isoelectric precipitation; the second method (samples *B*) is made washing the minced muscle with a buffer citrate-phosphate at pH 5. In both cases a decanter is used to collect the precipitate and then 8% of trehalose and 0.25 of sodium Tripoliphosphate are incorporated. The final pH in both surimis is about 7.

Samples *A* in raw, suwari and gel stage were designated *RA*, *SA* and *GA*, respectively, whereas their method *B* counterparts were named *RB*, *SB* and *GB*.

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) [2].

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 suwari samples 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 *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[3].

RESULTS

Stress sweep test

As it can be seen in Table 1, the limit stress values are bigger in gel samples than in suwari and raw ones, in both types of surimi, *A* and *B*. In general, surimi *A* presents larger maximum stress values than *B* except for raw sample which shows similar values.

Table 1. Stress and strain limit values for samples A and B at 10ºC.

	$\sigma_{máx}$ (Pa)	% $\gamma_{máx}$ ± S.D.
RA	204	0,90 ± 0,32
RB	256	1,26 ± 0,42
SA	685	2,72 ± 0,35
SB	547	3,33 ± 0,35
GA	1481	2,92 ± 0,19
GB	617	1,38 ± 0,29

On the other hand, the maximum strain values are bigger for suwari and gel samples, and they are similar in both kinds of surimi *A* and *B*. However, sample *GB* shows smaller limit strain values than *GA*.

Table 2 shows the shear modulus (*G*) for samples *A* and *B*. As it can be seen samples from method A presents higher *G* values than *B*. The relative difference between *B* and *A* increase in the raw-suwari transition (from 7 until 35%). However, the raw-gel stage change the relative difference is smaller than raw-suwari one (from 7 until 12%)

Table 2. Shear modulus values samples A and B at 10ºC.

	$(G \pm S.D.)\cdot 10^{-4}$ (Pa)
RA	2,049 ± 0,034
RB	1,895 ± 0,023
SA	2,511 ± 0,011
SB	1,639 ± 0,006
GA	5,099 ± 0,021
GB	4,459 ± 0,017

For that reason, we can say than samples from isoelectric precipitation method, developed more rigid samples than method *B* in both stages raw and gel.

Frequency sweep test

Figure 1 and 2 shows the viscoelastic moduli as a function of frequency, for surimi *A* and *B* in the three stages.

It can bee observed that suwari and raw samples present similar values of *G'* and *G''*, corresponding the biggest viscoelastic moduli values for gel samples. In general, samples *A* present higher viscoelastic moduli than ones from method *B*.

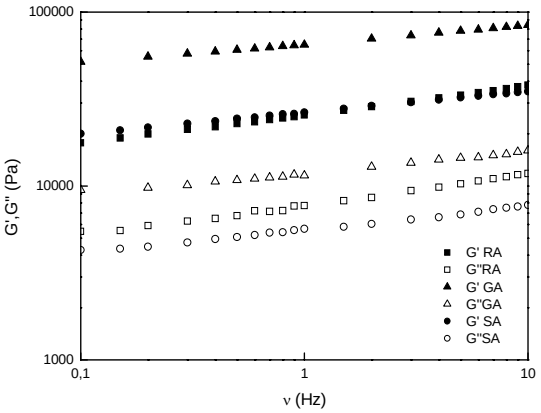

Figure 1. Mechanical spectra from frequency sweep test data. Samples *A* at 10ºC.

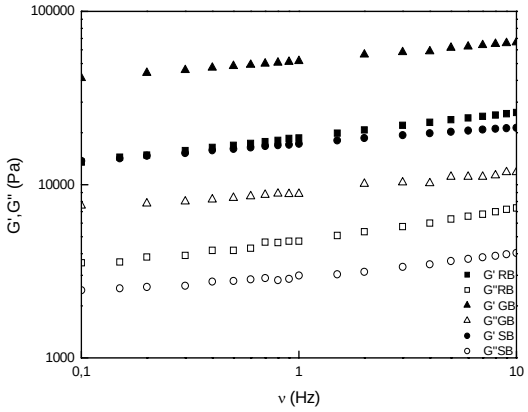

Figure 2. Mechanical spectra from frequency sweep test data. Samples *B* at 10ºC.

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

$$G^*(\omega) = A_\alpha \omega^\alpha \qquad (1)$$

We obtain A_α that measured the *strength* of the cross-linking polymer network and α describe the order of the relaxation function[4]. As it can be seen in Table 3 According to stress sweep test (Table 2), surimi *A* presents the highest viscoelastic moduli, this fact allow us to affirm that there is a little initial aggregation of the protein for surimi from method *A*.

Table 3. A_α and α values from eq.1 fit, samples *A* and *B*, at 10ºC.

	$(A_\alpha \pm S.D.)\cdot 10^{-4}$ Pa. $rad^n s^n$	α ± S.D.
RA	1,978 ± 0,003	0,1654 ± 0,0012
RB	1,479 ± 0,001	0,1458 ± 0,0007
SA	2,156 ± 0,0008	0,1235 ± 0,0003
SB	1,460 ± 0,0010	0,0982 ± 0,0006
GA	5,458 ± 0,005	0,1077 ± 0,0009
GB	4,359 ± 0,006	0,1040 ± 0,0012

Starting from relaxation exponent, it is possible to calculate the fractal dimension[5] (Eq. 2):

$$n = \frac{d\left(d+2-2d_f\right)}{2\left(d+2-d_f\right)} \qquad (2)$$

It can be observed that for samples *B*, there is a little increment from raw to suwari stages, in contrast with the suwari-gel transition (Table 4). Conversely, the fractal dimension for samples *A* shows higher rise in the raw-gel transition than *B*. We can say that the high *G** values of samples *A* in raw stage show the little initial protein aggregation in contrast with sample *RB* which presents more native protein content.

Table 4. Dimension fractal values from Eq. 2, samples *A* and *B*, at 10ºC.

	d_f ± S.D.
RA	2,354 ± 0,001
RB	2,372 ± 0,001
SA	2,393 ± 0,001
SB	2,415 ± 0,001
GA	2,407 ± 0,001
GB	2,410 ± 0,001

It should be necessary to stand out, that sample *GB* present slightly lower values of fractal dimension than *SB*, so the suwari sample might form a good conformational structure with 40ºC of heating. These results are corroborated with the low and similar values of *n'* and *n''* (Table 5) from the power law fit (Eq. 3 and 4)

$$G' = G_0^{'} \cdot \nu^{n'} \qquad (3)$$

$$G'' = G_0^{''} \cdot \nu^{n''} \qquad (4)$$

On the other hand, it is possible to say that for *RA* samples the more percentage of protein denaturation could origin local crystalline regions that provide rigid and brittle character, as we can see for the

highest A_α (Table 3), *n'* and *n''* parameters (Tabla 5).

Table 5. n' and n'' values from Eq. 3 and 4, samples A and B at 10ºC.

	n' ± *S.D.*	**n'' ± *S.D.***
RA	0,164 ± 0,0011	0,175 ± 0,003
RB	0,1444 ± 0,0006	0,165 ± 0,004
SA	0,1231 ± 0,0004	0,133 ± 0,002
SB	0,1060 ± 0,0005	0,108 ± 0,003
GA	0,1072 ± 0,0008	0,121 ± 0,003
GB	0,1040 ± 0,0011	0,105 ± 0,004

Creep and recovery

In Figure 3, it can be seen the evolution of the compliance *J(t)* for samples *GA* and *GB*, both present similar *J(t)* values. The creep compliance data values allowed us to obtain the parameters *S* (gel strength) and *n* (relaxation exponent)[6] starting from the equation 5:

$$G(t) = S \cdot t^{-n} \qquad (5)$$

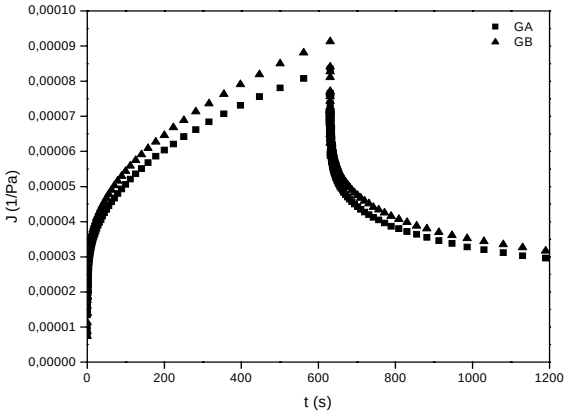

Figure 3. Compliance as a function of time, samples *GB* and *GA* at 10ºC.

As it can be observed in Table 6, samples *GA* present higher values of gel strength than *GB*, but the relaxation exponent shows identical values in both samples. For that reason, we can affirm that in spite of the higher *S* values of *GA*, both gels present the same structural organization.

Table 6. Gel strength and relaxation exponent values from eq.5 fit, samples *A* and *B*, at 10ºC.

	(*S ± *S.D.)·10 $^{-4}$ **Pa. s^n**	**n ± *S.D.***
GA	4,224 ± 0,018	0,169 ± 0,003
GB	3,863 ± 0,018	0,166 ± 0,003

CONCLUSIONS

Based on oscillatory test, it can be said that the viscoelastic moduli increase with the raw-gel transition, and these values are bigger in surimi from isoelectric protein precipitation than for method *B*. For that reason, we can say that there is a little initial aggregation of the protein in method *A*.

The fractal dimension shows similar results, the d_f values increase with the transition raw-gel. However, for samples from method *B* there is a change in the tendency, because of the bigger values of *SB* than *GB*, showing both samples similar conformational structure.

ACKNOWLEDGMENTS

The authors would like to acknowledge the support of CSIC (Instituto del Frío), directed by Dr. A. J. Borderías, toward this research work.

REFERENCES

1. Sánchez-Alonso, I., Careche, M. and Borderías, A.J. (2007), "Method for producing a functional protein concentrate from giant squid (*Dosidicus Gigas*) muscle", *Food Chemistry*, **100**, 48-54.

2. Collyer, A.A. & Clegg, D.W. (1998). "Rheological Measurements". 2nd ed. Chapman & Hall, London.

3. Deman, J. M. and Beers, A. M. (1987). "Fat crystal networks: structure and rheological properties". *Journal of Texture Studies* **18**, 303-318.

4. Moresi, M., Bruno, M. and Parente E. (2003), "Viscoelastic properties of microbial alginate gels by oscillatory dynamic test", *Journal of food engineering*, **64**, 179-186

5. Nyström, B., Kjøniksen, A. y Lindman B. (1996). "Effects of temperature, surfactant, and salt on the rheological behavior in semidilute aqueous systems of a nonionic cellulose ether". *Langmuir*, **12**, 3233-3240.

6. Lapasin, R. y Pricl S. (1999). "Rheology of industrial polysaccharides: Theory and applications". Aspen Publishers, Inc. Gaithersburg, Maryland.