Effects of hydrocolloids and high pressure - heating processing on minced fish gels

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Abstract

Multivariate statistical methods were applied to data sets of measured gelling properties of blue whiting mince with several hydrocolloids added (locust bean gum, guar gum, xanthan gum, carboxymethylcellulose, iota-carrageenan, kappa-carrageenan or alginate) induced under different pressure - time - temperature gelling conditions. The main differences between gels were attributed to the process, all the gels were classified in three clusters on the basis of gelling treatment: 1) high pressure at moderate heating; 2) high pressure at cold temperature; 3) heating at atmospheric pressure. Cluster 1 was characterised by very elastic, light gels with high water holding capacity. In cluster 2, gels presented high puncture test properties (breaking deformation, breaking force, work of penetration) and high cohesiveness and water holding capacity. Cluster 3 gels presented low penetration test properties and cohesiveness; high adhesiveness and hardness; high lightness and yellowness. Each previous cluster was subdivided to describe the gel properties between the hydrocolloid groups, attributing the differences mainly to yellowness (b^*), breaking deformation, breaking force and work of penetration.

Key words: gel, mince, high pressure, thermal treatment, hydrocolloid, multivariate analysis.

INTRODUCTION

Starch, carrageenans and alginate are the most useful hydrocolloids added to mince fish and / or surimi in order to modify gelling characteristics of final restructured products [1]. Other hydrocolloids, usually gums extracted from seaweed or seeds, also exhibit important functional properties, however scarcely study on the gelling properties of the fish gels. Pérez-Mateos and Montero [2] recently reported the effects of different concentrations of divers gums added to blue whiting mince and subjected to heat treatment. In general, the authors found that more than 0.5 % of hydrocolloid significantly reduced rheological properties, but increased water holding capacity.

In recent years, some studies have been done on gelation of fish minces using high-pressure treatments. These studies have reported advantages over conventional treatments to be derived from the combined effects of pressurising and heating [3-6]. The effects of high pressure treatment will vary mainly according to the processing conditions (pressure - time - temperature), functional properties of fish mince, and type of species. Hardly any studies have been done on the effect of gelling and water binding substances on pressure-induced mince gels. Fernández et al. [7] and Fernández-Martín et al. [8] have reported the influence of polysaccharides (iota-carrageenan and starch) under high pressure in meat systems. There is also an earlier study of gelation of blue whiting muscle of poor functional quality with addition of starch under high pressure treatment [5].

The present work is an attempt to identify the characteristics of the gels (mechanical properties, water holding capacity and colour) with respect to various compositional variables: hydrocolloids (locust bean, guar, xanthan, carboxymethylcellulose, iota-carrageenan, kappa-carrageenan, alginate) and process parameters (pressure, time, temperature) as a whole in order to clarify the role of each one of them.

MATERIALS AND METHODS

5 Blue whiting (Micromesistius poutassou Risso) used in this study was caught off the Cantabrian coast in November. Average size was 22.2 ± 1.8 cm and average weight 101.1 ± 22.3 g. The proximate composition (%) of mince was performed according to AOAC procedures [9] and crude fat by Bligh and Dyer [10]: crude protein 13.25 ± 0.31 , moisture 81.75 ± 0.71 , crude fat 0.16 ± 0.03 and ash 0.40 ± 0.05 (analyses do not show cryoprotectants
10 added).

Mince and gel preparation. Fish were headed, gutted and washed. Skin and bones were removed with a deboning machine (Baader 694, Lübeck, Germany). The resulting mince was washed in a solution of NaCl (0.2 %) at 0-3 °C, proportion 3:1 (solution:minced muscle), first
15 with constant stirring for 10 min then without stirring for another 10 min. After draining, excess water was removed using a screw press (Baader 523, Lübeck, Germany). Sorbitol (4 %) and tripolyphosphate (0.2 %) were added as cryoprotectants. The mince was immediately vacuum-packed in bags (Cryovac BB-1, Grace, Spain) and frozen in a plate-freezer (Sabroe SMC, Denmark). The bags were stored at -80 °C in a freezer cabinet (Revco ULT, Giralt,
20 Revco Scientific, Inc., Asheville, N.C., USA) in order to minimize alteration during frozen storage up to gel preparation.

Washed blue whiting mince was tempered in a chilled room and placed in a refrigerated vacuum homogenizer (Stephan UM5, Stephan u. Söhne GmbH & Co., Germany). It was
25 ground for 1 min at high speed. Sodium chloride (1 % w/w) in gel (Panreac, Montplet & Esteban S.A., Barcelona, Spain) was added and homogenized for 3 min at slow speed. Then the hydrocolloid was added at a final concentration of 0.5 % (1 % in the case of locust bean

gum) with crushed ice to give the required final gel moisture content (80 %) based on previous work of Pérez-Mateos and Montero [2]. The hydrocolloids were supplied by SKW Biosystems (Rubí, Spain): locust bean gum as Viscogum™ BE, guar gum as FFH-200, xanthan gum as Satiaxane™ CX90, sodium carboxymethylcellulose as Tylopur™ C10000, iota-carrageenan Satiagel™ RPT25, kappa-carrageenan as Satiagel™ RPT8, sodium alginate as Satialgine™ S1100. The extra salts added were NaCl and KCl in accordance with the results of Pérez-Mateos [11]. The homogenate was beaten slowly for 6 min under vacuum, keeping sample temperature below 10 °C. Batters were stuffed into flexible plastic casings (Krehalon Soplaril, Barcelona, Spain) of 40 µm thickness and 3.5 cm diam. and subjected to gelation treatment.

The following treatments were applied, as described in Pérez-Mateos and Montero [12]: 200 MPa, <10 °C, 10 min (gel L) and 375 MPa, 37 °C, 20 min (gel H). These authors reported the characteristics of the gels without gum added using a mince with similar capacity of gelation to the one used in the actual work. The control gel was obtained by traditional gelation at atmospheric pressure under heat treatment: 37 °C, 30 min followed by 90 °C, 50 min (gel T). High - pressure treatments were performed in a high pressure pilot unit (ACB 665, Gec Alsthom, Nantes, France) where the temperature of the immersion medium was controlled via a thermo-couple. All the casings were immediately cooled with water at 0 °C and stored in a cold room at 4 °C for 24 hours before analysis.

Samples were removed from their casings, cut (3.5 cm diameter, 3 cm height) and tempered at 20 °C. The analyses were determined as described in Pérez-Mateos and Montero [2] made at least six replications: folding test resistance of a slice folded over twice (score 1-5); puncture test (breaking deformation, breaking force, work of penetration) with a round-ended stainless steel plunger (Ø=5 mm) at a speed of 10 mm / min using a load-cell of 100 N; Texture Profile Analysis (hardness, adhesiveness, cohesiveness) at a deformation rate of 50 mm / min using

a cylindrical plunger ($\varnothing = 58$ mm) adapted to a load-cell of 5 kN compressed to 60 %; and stress-relaxation test after 1 min of relaxation (elasticity). Also colour (L^* , a^* , b^*) using the CIE Lab scale (D65/10°) at least six replications were performed and water holding capacity determined by centrifuge method (1.5 g at 4000g for 15 min at 20 °C) at least in triplicate [2].

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Statistical analysis. All descriptive statistics and statistical tests were performed using the BMDP computer program (BMDP Statistical Software, Inc., Cork Technology Park, Cork, Ireland). Each multivariate analysis was performed on all data values, obtained from the different gelation treatments for each hydrocolloid studied and the control gel without hydrocolloid added, treated as a whole set. Correlation among properties was calculated. Factorial analysis by principal component analysis (BMDP 4M) was done with Varimax rotation and the results were subjected to non hierarchical cluster analysis (BMDP KM) and stepwise discriminate analysis (BMDP 7M).

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15 **RESULTS AND DISCUSSION**

The large number of characteristics observed (mechanical properties, water holding capacity and colour) for each hydrocolloid (locust bean, guar, xanthan, carboxymethylcellulose, iota-carrageenan, kappa-carrageenan, alginate) under the different treatments (pressure, time, temperature) make difficult to reach conclusions about relationships among the variables (properties of gels) or to identify in which way the variable modified the characteristics of the gel. Multivariate analysis was used in order to facilitate these studies.

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25 **Factor analysis**

Exploratory factor analysis was used to obtain information about interrelationships between the

twelve characteristics of 21 different types of gels (7 types of hydrocolloids treated by 3 different treatment). In the correlation matrix, the overall variation presented in the data set ($n = 72$) was summarised by three factors or principal components, which accounted for 91.52 % of the variance (Table 1). Variables with loading on the same factor tended to be highly correlated with each other; while those variables which belonged to different factors tended to be less correlated. The first factor explained half of the total variance (50.36 %) and it was represented largely by the variables determined in the penetration assay (breaking deformation, breaking force, work of penetration), which it were exclusive to this factor. It also included the properties obtained in the stress-relaxation test, such as cohesiveness and elasticity, which evolved in opposite directions, and other physical properties such as lightness. This seems to mean that gels, although they were capable of retaining their structure under a deforming force (high cohesiveness and high breaking force), they failed to recover after compression (low elasticity). The negative correlation between breaking deformation and elasticity seems in reasonable agreement with previous results reported in gels of blue whiting without hydrocolloids [12], in spite of the fact that both properties were obtained by different techniques, namely puncture test and compression test.

In the second factor (26.97 %), compression properties such as adhesiveness and hardness were the most significant; with negative loading, water holding capacity was also significant, as was breaking deformation. This suggests that the connecting forces of the gel network were strong (high hardness) and capable of interacting with the exterior (high adhesiveness), with little deformability. The colour parameters (redness and yellowness) were the main contributors to the third factor (22.67 % of total variance), redness being exclusive to this factor.

Cluster analyses

Cluster analyses were performed on the basis of the factors defined by factor loadings. In figure 1 is shown a graph where canonical variables were a function of gel properties which best discriminates among groups along the X-axis; while the second canonical variable discriminates groups along the Y-axis. Three groups were found with homogeneous distribution of elements totally defined by the different treatments; although in cluster 2 there appear to be two subclusters. The characteristics of each cluster were defined in the distribution profile of these variables and the mean values of each variables for different cluster (Fig. 2). These gels were distinguished mainly by their cohesiveness ($F = 566.5$) and their elasticity ($F = 106.9$) and, to a lesser extent, by their adhesiveness ($F = 22.5$), breaking force ($F = 13.3$) and colour (b^* : $F = 8.1$, a^* : $F = 4.4$).

Cluster 1 was composed of all the gels induced by high pressure and moderate heating (gel H: 375 MPa, 37 °C, 20 min), which were very elastic and light with high water holding capacity.

Cluster 2 was composed of all the gels induced by high pressure at low temperature (gel L: 200 MPa, <10 °C, 10 min); these gels presented high values for the penetration test properties (breaking deformation, breaking strength, work of penetration), and also high adhesiveness and water holding capacity. Cluster 3 was composed of all the gels induced by heating at atmospheric pressure (gel T: 37 °C, 30 min/ 90 °C, 50 min); unlike the previous cluster, these gels presented low values for the penetration test properties and cohesiveness, but high adhesiveness and hardness. Also, heat induced gels were light with a slight yellow tinge.

The efficiency of the discrimination function was demonstrated to be 100 % by the Jack-knife procedure. The reason for this clear differentiation in gel characteristics by gelling treatment may be that denaturation and aggregation were induced in different ways by the different pressure-time-temperature combinations. Fernández-Martín, Pérez-Mateos and Montero [6] recently reported that at non-denaturing temperature, the protein unfolding effect was larger

the higher pressure, and that at denaturing temperature, pressure protected fish protein from subsequent thermal denaturation.

Another cluster analysis was done in each previous cluster to describe the gel properties between the hydrocolloid groups. Thus, in cluster 1, the gels induced by high pressure and moderate heating (gel H: 375 MPa, 37 °C, 20 min) were classified by type of hydrocolloid in three subclusters. In figure 3, the distribution profile of characteristic and the mean value are shown. These gels were distinguished chiefly by yellowness (b^*) and breaking deformation (statistical values: 42.5 and 28.9, respectively), and to a lesser extent by hardness ($F = 9.1$).

Subcluster 1.1 was composed mainly of the gels containing alginate; the principal characteristics of these gels were high adhesiveness, hardness and water holding capacity, and their colour values (high lightness, redness and yellowness). Subcluster 1.2 contained those gels having higher than average properties (asterisks in Figure 3 indicate mean values of the characteristics studied) except for lower adhesiveness. This group was principally formed by gels containing thickeners hydrocolloids: locust bean gum, guar gum, xanthan gum and carboxymethylcellulose. In subcluster 1.3, characteristics of gels were generally lower than average except for higher adhesiveness and hardness, it was composed mainly of gels containing iota-carrageenan and kappa-carrageenan and a minority of gels containing no hydrocolloids. This suggests that under these gelling conditions, the various hydrocolloids behaved differently. In general, it was possible to distinguish on the one hand the thickeners (galactomanans, xanthan gum and carboxymethylcellulose) and, on the other hand, the carrageenans (iota and kappa) and sodium alginate.

The gels induced by high pressure at chilling temperature (200 MPa, < 10 °C, 10 min) also fell into different categories depending on the type of hydrocolloid added. Again, three subclusters were obtained as it is shown in the distribution profile of characteristics (Figure 4). and the mean value respectively for the corresponding subcluster. As in the previous treatment, the

clusters were again differentiated by breaking force ($F = 59.5$) and yellowness (b^*) ($F = 31.9$), and moreover by adhesiveness ($F = 28.3$) and hardness ($F = 5.2$). Subcluster 2.1 was composed of the gels with added locust bean gum, guar gum and iota-carrageenan and the gels with no added hydrocolloids, which presented high values of breaking force and work of penetration, hardness and adhesiveness. In subcluster 2.2, the gels presented high elasticity, low adhesiveness and low values for the penetration test properties (breaking deformation, breaking force and work of penetration); they consisted mainly of gels containing xanthan gum and kappa-carrageenan. Unlike the previous one, in subcluster 2.3 the gels were highly deformable and cohesive with high water holding capacity, lightness and yellowness (b^*); they consisted mainly of gels containing carboxymethylcellulose and sodium alginate. Under these gelling conditions the groupings were different from those of the gels induced by high pressure and moderate heating, which suggests that the behaviour of the hydrocolloids inside the protein matrix differ according to the treatment applied.

In the case of the gels induced by heating ($37\text{ }^{\circ}\text{C}$ 30 min / $90\text{ }^{\circ}\text{C}$ 50 min) at atmospheric pressure (Figure 5), the clusters were differentiated chiefly by work of penetration ($F = 54.3$) and yellowness (b^*) ($F = 31.6$), and to a lesser extent by cohesiveness ($F = 4.7$).

Subcluster 3.1 was composed mainly of gels containing locust bean gum and partially by gels containing iota-carrageenan; in general, these gels presented higher rheological characteristics than the other heat-induced gels. Subcluster 3.2 was characterized chiefly by high values of elasticity and colour (L^* , a^* , b^*), and generally by high water holding capacity. It was composed mainly of gels containing carboxymethylcellulose and sodium alginate, with some cases containing xanthan gum. Subcluster 3.3 was composed of gels with intermediate characteristics, consisted mainly of gels containing guar gum, kappa-carrageenan and control without hydrocolloids added, with a minority containing xanthan gum or iota-carrageenan. These groupings were different from the groupings of pressure-induced gels, bearing out the

different behaviour of the hydrocolloids in the protein matrix depending on the treatment used.

The multivariate analysis has proved to be a valuable tool for evaluating and quantifying the influences of the variables in the effect of high pressure- heating treatments for processing fish mince gels containing hydrocolloid. These findings can be useful to get a desirable texture and stabilization of water in fish muscle gels. Gelling properties of fish mince were enhanced by addition of various types of hydrocolloids, and the behaviour of these properties differed for each treatment and also for each ingredient under different treatments.

The gels were grouped on the basis of gelling treatment: high pressure and moderate heating, high pressure at cold temperatures and heating at atmospheric pressure. The main differences, attributed to the pressure - time - temperature combination, were in cohesiveness, elasticity and adhesiveness. Whereas the differences attributed to the hydrocolloid varied according to the gelling treatment used.

As regards high-pressure, cold-pressurized gelation opens up a number of further possibilities, like the incorporation of functional ingredients for nutritional purposes, such as bioactive compounds (vitamins, fatty acids, antioxidants). Due to the fact that high pressure is quite less destructive technology in comparison with heat treatment, allowing that termolabil compounds remains more active after pressurizing at cold temperature than after heating.

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