Effect of setting time on the rheological properties of suwari gels made with squid surimi with added Konjac glucomannan

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Introduction
Surimi, consisting of a concentrate of salt-soluble myofibrillar proteins, has gelling properties that make it useful as a base in gel-based food products. Alaska pollock (Theragra chalcogramma) is the species that produces the best nominal quality of surimi (1). Research has shown that a cephalopod such as giant squid (Dosidicus gigas) may also be used if it is subjected to specific chemical treatments (2). Two patents have been reported dealing with squid surimi (3, 4), the first based on acid solubilization followed by isoelectric protein precipitation, and the second on muscle washing with an acid solution. The rheological characteristics of surimi gels depend on the temperature and heating time applied to the minced muscle after mixing with NaCl to solubilize the proteins. When subjected to T<40°C, the resulting gel, called “suwari”, is soft, elastic and cohesive. This kind of gel preserves the flavour and colour of raw fish muscle. During setting in this temperature range, myosin heavy chain (MHC) becomes polymerized through the formation of non-disulphide covalent cross-links, catalysed by an endogenous transglutaminase (TGase) (1).

Gelling characteristics of surimi from giant squid (D. gigas) can be enhanced using an aqueous dispersion of a polysaccharide, such as Konjac glucomannan (KGM). Moreover Iglesias- Otero et al. (2010) (5) reported that addition of 1% of aqueous dispersion of KGM-10% wt (ADK) at pH=8.5 in squid surimi noticeably improved the thermal gelation profile. A previous paper (6) analysed the effect of the T increase at a fixed heating time. The aim of the present study was to determine the influence of setting time at a fixed T=40°C on the rheological properties, under large and small deformations, of suwari gels made with giant squid (D. gigas) surimi processed by isoelectric precipitation with 1% added ADK (10% wt).

Experimental Methods
The squid surimi was produced by a method patented by (3). Alaska pollock (T. chalcogramma) surimi (grade A) was supplied by a local factory and was analysed as a reference of a very good gel. The suwari gels used in this study were: A samples are neutral suwari gels from A. pollock surimi grade A; B samples are from giant squid (D. gigas) surimi + 1% ADK at pH=8.5 (this preparation is described in (5), and C are control samples, i.e. neutral suwari gels made from squid surimi without ADK. The raw pastes were placed in cylindrical steel cells in a water-bath (Memmert WB 10.) at 40°C for 0.5, 1, 2 and 4 hours. Afterwards the cells with the sample inside were placed in a water-ice slurry and finally kept refrigerated at 7°C for one day. Puncture tests were performed at 20°C to breaking point, using a TA-XT2 Texture Analyser (SMS, Surrey, UK) with a 5 mm–diameter round–ended metal probe. Crosshead speed was 1 mm/s, and a 2 kg load cell was used. The load as breaking force (BF) and the depth of depression as breaking deformation (BD) were recorded.
From these data we calculated the ratio BF/BD; this gives the fracture constant (Ki), which provides a measure of relative rigidity of gels at the failure point. All determinations were carried out on at least six replicates.

Small amplitude oscillatory shear (SAOS) data were gathered using a Bohlin CVO controlled stress rheometer (Bohlin Instruments, Inc. Cranbury, NJ). The measurements were carried out using a parallel plate (20 mm in diameter and 1 mm gap). The temperature of the lower plate was kept at 10.0 °C ± 0.1. Frequency sweeps were performed over the range 0.1–10 Hz, keeping the γ=0.5% constant within the LVE region. Transient tests were carried out applying a constant shear stress (σ) within the linear viscoelastic (LVE) range for 600s; after that, when removing the load other 600s was the recovery time to obtain the reformation curve.

Results and Discussion

Effect of setting time on textural properties of suwari gels

Figure 1 shows the effect of setting time on the rigidity of suwari gels A, B and C. The rigidity of B samples continuously increased with increasing setting time. In C gels, Kr values also increased at longer times, particularly 4 hours. Conversely, in A suwari gels Kr values were practically independent of heating time. B and C gels (squid surimi) were more rigid than A gel (A. Pollock) at any setting time. The addition of 1% of ADK (B gel) at any fixed time caused a much greater increase of rigidity, as evidenced by the notable increase of Ki in B with respect to C suwari gels, which was significant for 1, 2 and 4 hours (Figure 1). This increase of rigidity with time showed the particular packing effect caused by the KGM in squid-suwari gels. However in A suwari gels heated at 40°C the overall rigidity was independent of the setting time. It therefore seems that non-disulphide covalent protein-protein bonds like ε-(γ-glutamyl) lysine dipeptide rendered the firmness of the A suwari-network equally time-stable.

Figure 1. Influence of setting time on the fracture constant of suwari gels C (control) A (A.p.surimi), B (squid surimi+1%ADK). T= 20°C

Linear viscoelastic (LVE) range

Stress sweeps were used to determine the limit values of stress (σmax) and strain (γmax) in suwari gels for each setting time. Note that during the first hour of setting there were two opposite trends in samples A and B relative to those at 0.5 h: on the one hand, in A suwari gel σmax and γmax both significantly increased (p<0.05), reflecting an improvement in the rheological quality of suwari gel A. Conversely, in samples B the same time produced a significant decrease in both σmax (Table 1) and γmax (Figure 2), indicating an increase of stiffness in the B suwari gel, resulting in a less flexible and more unstable network (7).

Table 1. Setting time effect on the stress amplitudes, σmax (kPa), of suwari gels made with the three kinds of surimi. T=10°C.

<table>
<thead>
<tr>
<th>t(hour)</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.365±0.037a</td>
<td>1.40±0.14b</td>
<td>1.22±0.12c</td>
</tr>
<tr>
<td>1</td>
<td>0.719±0.072a</td>
<td>0.982±0.098d</td>
<td>1.31±0.13e</td>
</tr>
<tr>
<td>2</td>
<td>0.456±0.046a</td>
<td>1.28±0.13f</td>
<td>1.18±0.12g</td>
</tr>
<tr>
<td>4</td>
<td>0.467±0.047a</td>
<td>1.44±0.14e</td>
<td>1.14±0.14f</td>
</tr>
</tbody>
</table>

**a** Different small letters in the same column indicate significant differences with setting time for each sample (P<0.05).

**A:** Different capital letters in the same row indicate significant differences among samples at fixed setting time (P<0.05).

However, in samples C, σmax and γmax remained practically constant over the same time (1 hour). From t> 1 hour to 2 hours the trends of σmax for A and B samples were again opposite, but in a different sense than during the first hour: in A sample σmax and γmax decreased, while in B...
suwari gel both parameters increased (Table 1 and Figure 2). In C suwari gel $\gamma_{\text{max}}$ significantly decreased (Figure 2) while $\sigma_{\text{max}}$ remained almost constant (Table 1).

The highest value of factor $Q$ was found in A suwari gel after 1 hour of setting (Figure 3). This result, together with the high $\gamma_{\text{max}}$ (Figure 2), shows that 1 hour was an optimum setting time to improve the functional properties of actomyosin in A. pollock surimi and so make suwari gels of better quality. The benefit of adding 1% of ADK as an ingredient to squid surimi (B gel) can be seen already at 0.5 h of setting, in that the factor $Q$ was significantly higher in B gel than in C gel. In B sample, from t=1h factor $Q$ retained practically the same value as at 0.5 h. (Figure 3), showing the time stability effect exerted by ADK during heating. Conversely, in C sample between 1 and 2 h, factor $Q$ diminished dramatically, increasing finally at 4 h (Figure 3). This behaviour showed the structural instability of the C suwari network due to initial aggregation of myofibrillar protein (5).

The relaxation moduli $G(t)$ can be derived from creep compliances $J(t)$ (data not shown) Thus, the equation of Winter and Chambon (9) can be used to calculate other parameters related to gel strength $(S)$, and also to the relaxation exponent $(n)$, by:

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

(3)

Where $S$ (Pa·s$^n$) depends on the strength of the network and $n$ is related to the connectivity degree in gels (10).

In general, from 0.5 to 4 hours, the gel strength increased with increasing setting time, proportionately least in samples A (39%), followed by C (59%), and most in B suwari gels (133%) (Table 2). This indicates that 1% of ADK with increased heating time produced a stronger network, which is consistent with the fact that $K_i$ was highest in puncture tests (Figure 1) and $\gamma_{\text{max}}$ was lowest in stress sweeps (Figure 2). The
explanation for this result may be that after 4 hours at 40°C, a large number of polymer-water hydrogen bonds had been broken, resulting in a new rearrangement of water molecules in the network. Thus, 1% ADK may help to reinforce protein-protein hydrophobic interactions even with low-temperature setting (1).

Table 3. Setting time effect on $n$ values (equation 3) for the three suwari gels. $T=10^\circ C$.

<table>
<thead>
<tr>
<th>(hour)</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.164±0.002</td>
<td>0.139±0.002</td>
<td>0.161±0.002</td>
</tr>
<tr>
<td>1</td>
<td>0.156±0.002</td>
<td>0.150±0.002</td>
<td>0.167±0.002</td>
</tr>
<tr>
<td>2</td>
<td>0.164±0.002</td>
<td>0.175±0.002</td>
<td>0.173±0.002</td>
</tr>
<tr>
<td>4</td>
<td>0.163±0.002</td>
<td>0.162±0.002</td>
<td>0.165±0.002</td>
</tr>
</tbody>
</table>

Values are given as mean values ± standard deviation of fit parameters.

Thus, ADK could form a parallel network within the principal (actomyosin) network in B suwari gel. Increasing time may help the KGM network to settle, resulting in a strong structure with little order and high gel strength. The low level of conformational order is reflected in the high $n$ value in B suwari gel (similar to A and C samples) after 4 hours of heating (Table 3). When the number of cross-links diminishes $n$ increases, and so a discontinuous and heterogeneous protein-polysaccharide matrix may form at high setting times. Conversely, in B sample, $n$ was the lowest after 0.5 hour of setting (Table 3). This result corroborates the fact that 1% ADK improved the degree of connectivity in the suwari network at shorter times. Thus, 0.5 hour is a long enough setting time to improve suwari gels made from squid surimi.

Conclusions

0.5 hour setting at T=40°C was an optimum time for improving the structural quality of suwari gels made with squid surimi (which has poor gelling ability) +1% of a 10% aqueous dispersion of glucomannan at pH=8.5. One hour was the best setting time for suwari gels made from Alaska Pollock surimi

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References


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