FACTORS AFFECTING THE RHEOLOGICAL PROPERTIES OF GELS MADE FROM HOKI (*MACRURONUS NOVAEZELANDIAE*)

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ABSTRACT

Hoki (*Macruronus novaezelandiae*) is an important commercial fish in the New Zealand Exclusive Economic Zone. The resource remains underutilized with only a small proportion of the 250,000 tonnes Total Allowable Catch presently being made into added value products. There is interest in producing surimi, a refined, stabilized form of fish mince, from hoki. Surimi is an intermediate raw material used for the production of a range of fabricated foods. The rheological properties of these gel-based foods are of key importance for their consumer acceptability. The quality of surimi is determined predominantly by the gel-forming ability of the myofibrillar protein of the raw material fish used in the process. These properties change with chilled and frozen storage of the fish.

The objectives of this study are to develop methodology to test the gel-forming ability of surimi; to investigate the changes in gel-forming ability of hoki with chilled and frozen storage, and to evaluate the rheological methods used in these studies. The implications with respect to a domestic surimi industry are discussed.

The rheological properties of gels made from hoki stored for various times, chilled or frozen, were determined using two failure tests, namely the puncture test and the torsion test. The puncture test is an empirical method commonly used in the surimi industry, where a 5 mm diameter spherical probe is driven into the gel at constant plunger speed. The force and deformation at failure are used to describe the mechanical properties of the gels. The torsion test is a fundamental method whereby a pure shear state is obtained by applying a twisting moment about a central axis. The shear stress and true strain at failure are calculated and used to follow the changes in gel properties with time.

The strength of gels decreased as the fish spoiled on chilled storage . The decline appears to be slower than that reported for other fish such as Alaska pollock. Even after 10 days storage the gel strength was such that hoki would still have excellent gelling properties based on Japanese classification systems.

The storage of headed and gutted hoki at -29°C resulted in a significant loss of gel-forming properties over time. The strength of gels were less than the minimum for Japanese ship-processed surimi after about 100 days storage. Hoki appears to lose gel-forming ability with frozen storage at a similar rate to that of Alaska pollock. Measurement of the pH and formaldehyde concentration of the flesh were good indicators of the gel-forming ability of frozen stored hoki. The true strain at failure showed the highest correlation with storage time.

Finally, the puncture and torsion tests were evaluated with respect to their use for specifying surimi quality. Specifically their precision, cost, convenience and correlation with a sensory method, were assessed. The results of the storage studies were pooled to provide data covering a wide range of gel textures.

Parameters from both tests showed significant correlations with the sensory method, with the puncture force showing the greatest overall correlation. Both methods showed good response to changes in fish quality.

There was a large error associated with the puncture force value when firm gels were tested. Standard deviations of up to 25% of the mean were measured. The other parameters for both tests gave standard deviations of about 10%. This demonstrated the high error normally associated with failure testing, and the difference between a point test where the applied force is concentrated over a small area and the torsion test where the stress is applied over a larger area hence averaging the effect small defects may have on failure of the sample.

It was concluded that the puncture test is suitable for routine quality testing of surimi, however both the force and deformation results should be reported. For research and when more accurate specification of quality is needed then the torsion test would be more appropriate. Whichever method is used, it is imperative that the preparation and testing of surimi be carried out in a consistent and uniform manner to allow comparison and communication of results. There is a need for a standard industry-wide method for testing the gel-forming ability of surimi.

To make consistent surimi an on-shore operation would require strict control of fish quality. Measurement of fish freshness based on organoleptic assessment and the K value may be a useful basis for a hoki surimi quality assessment program. It is probable that the loss of functional gel-forming ability of hoki during frozen storage at -29°C would be too fast to allow the use of frozen hoki for making surimi over an extended period in a commercial operation. Decreasing the storage temperature may extend the useful storage life, but this would have to be balanced against the increased capital and running costs of storage at these lower temperatures.

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1. INTRODUCTION

1.1 The Hoki Resource

The primary objective of the New Zealand fishing industry is to add value to New Zealands fish resources. The declaration of the 320 km Exclusive Economic Zone (EEZ) in 1978, gave New Zealand the fourth largest EEZ in the world. Within this area hoki (*Macruronus novaezelandiae*) is the dominant commercial fish specie (Patchell,1986). Since 1978 the catch of hoki has been steadily increasing (Figure 1.1), however hoki remains an underutilized resource with only 4,543 tonnes of frozen fillets and 16,000 tonnes of other forms of frozen hoki exported in1987 (Anon, 1988). In 1987 the Total Allowable Catch for hoki was increased to 250,000 tonnes per annum based on an estimate of the biomass of adult fish (over 65 cm in length) of 1.25 million tonnes and a productivity (based on age structure of the population) of 20%. This estimate of the hoki biomass is considered conservative (Sullivan, 1988).

1.2 Traditional Fish Products From Hoki

Hoki is a difficult fish to process into fillet based products. The flesh is soft, and is prone to gaping, that is separation of the muscle segments, during chilled storage (Bremner and Hallett,1985). Gaping of fillets can result in large processing losses and poor quality product. Hoki is also susceptible to severe bruising during harvesting which increases labour costs associated with trimming operations when manufacturing premium fillet products, and reducing yields.

Hoki is capable of producing formaldehyde on frozen storage from the enzymic breakdown of trimethylamine oxide. The enzyme responsible, trimethylamine oxidase (TMAOase), is active in frozen storage and under these conditions the formaldehyde formed can react with the myofibrillar proteins forming inter and intramolecular hydrogen bonds between the proteins

(Bremner,1980). Rapid denaturation of the myofibrillar proteins during frozen storage is typical of fish in which formaldehyde is produced. This results in a flesh texture which is tough, dry and fibrous, thereby reducing the consumer acceptability of frozen hoki products.

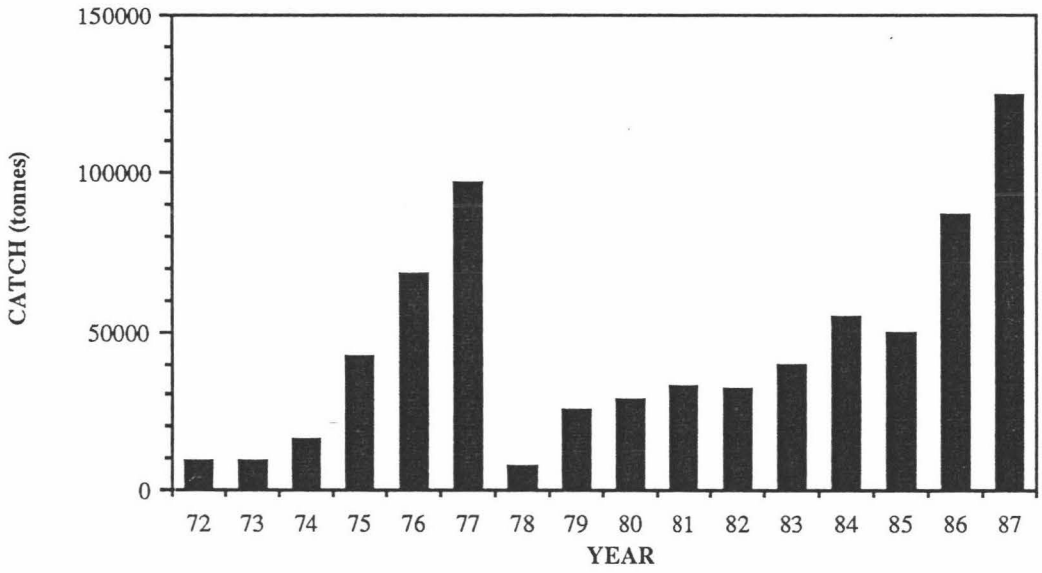

Figure 1.1 Reported hoki catch for New Zealand waters for the years 1972 to 1987 (From Robertson, 1986)

1.3 Surimi, A New Product From Hoki

There is a need for alternative processed forms of hoki to enable the resource to be more fully utilized. There is much interest in the production of surimi from hoki. Surimi is a Japanese term for stabilized refined fish mince. It is made from mince that has been washed to remove fat and undesirable matter (such as blood, pigments and odorous substances), and mixed with cryoprotectants (such as sugar and sorbitol) for a good frozen storage life (Martin, 1986). Deboning ensures efficient recovery of edible meat while washing and addition of cryoprotectants improves protein stability during frozen storage. It is a semi-stable intermediate raw material in which the functional proteins of fish muscle, mainly actomyosin, are stored for later manufacture into various fabricated consumer foods.

The flesh of hoki is white and the fish is reported to be capable of forming strong cohesive gels when comminuted with salt and heat-set, functional properties which are prerequisites for making high quality surimi (Sonu, 1986; Iwata and Yamada,1969). Hoki surimi is seen as a potential large volume alternative to the traditional products of fish block and fish sticks.

In Japan, the development of surimi facilitated the expansion of a large scale food manufacturing industry that uses surimi as a base material. The surimi is comminuted with salt to form a sol into which other ingredients such as water, starch and flavourings are mixed, the resultant paste is then formed and heat-set to form a thermo-irreversible protein gel. The generic name for these products is *neriseihin* or *kamaboko* , approximately one million tonnes are produced each year in Japan (Anon, 1983).

Surimi-based fabricated foods rely on the functional properties of fish myofibrillar proteins to form a stable gel network and so create various textures in a product system. Recently, seafood analogues made from surimi have been developed that simulate the texture of high value seafoods, such as the fibrous meat from

Alaska king crab and scollops. The texture of these products has been identified as a critical preference factor for their acceptability (Hamann and Lanier,1986) . Thus the rheological properties of these products and the control of these properties is of key importance.

1.4 Testing The Rheological Properties Of Surimi

Rheological tests form the basis of methods to test the quality of surimi. In particular a puncture test is used for quality control purposes in the Japanese industry. Recently, a fundamental method, the torsion test, has been suggested for use in surimi quality testing (Lanier et al.,1985). Evaluation of the advantages and disadvantages of each rheological method for use in industry is needed.

1.5 Factors Influencing Surimi Quality

The primary concern of the surimi manufacturing operation is to ensure the quality of the product with respect to its functional properties, in particular gel-forming ability. This property is greatest when the myofibrillar proteins are in an undenatured form, hence much of the processing effort is directed at maintaining the fish muscle proteins in their native state. Wide variations in the gel-forming properties of muscle proteins from different species of fish have been noted (Shimizu et al, 1981). Although, it is reported that hoki can be made into high quality surimi there is a need for further investigation of the variables that will influence the rheological properties of gels made from hoki, such as the effects of chilled and frozen storage on gel-forming ability.

In Japan, because of the distance from the main fishing grounds, most of the high quality surimi is made at sea on-board factory vessels. Hoki however, is caught in large quantities close to land. Therefore, the opportunity is greater for shore processing of surimi, with consequent lower production costs than at-sea

processing. It is uncertain how such an operation would affect surimi quality because the fish would have to be stored in a chilled condition before processing. The possibility of utilizing frozen hoki for the production of surimi is also of interest as this would enable a shore-based surimi operation to operate throughout the year. There is a need for more knowledge of the relationship between fish quality and surimi quality with respect to hoki.

The objectives of this study are:

1. To develop methodology to test the gel-forming ability of surimi,

2. To investigate the changes in gel-forming ability of hoki with storage time in ice,

3. To investigate the changes in gel-forming ability of hoki with frozen storage time and,

4. To evaluate the rheological methods used in these studies.

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2. LITERATURE REVIEW

2.1 Introduction

Fish myofibrillar proteins function as a texture and structure building component in various fabricated seafoods. The gels formed by comminution of these proteins in the presence of salt and then heat setting the resultant sol, confer the textural properties important for the consumer acceptability of these products (Hamann and Lanier, 1986). It is necessary therefore, to develop an understanding of the mechanical attributes of the final heat-set gel products and their relationship to sensory texture. The prediction and control of texture in product development would allow processors to obtain products with optimum consumer acceptability (Hamann, 1983).

This review therefore seeks to present information on rheological theory and methods with respect to muscle protein gel systems. Then large deformation to failure methods with application to surimi quality testing are reviewed.

2.2 Food Texture

Texture can be considered as the composite of the structural elements of food and the manner in which it registers with physiological senses (Szczesniak, 1963). It is the subjective assessment of a food and is made up of the important elements of; the physical structure of the material (its geometry) and the way the material handles and feels in the mouth (its mechanical and surface properties). Texture is a subjective attribute of a food and can only be measured using subjective tests such as sensory profiling. Thus texture is a multi-faceted concept and it is unlikely that a single instrument or test can adequately describe all textural characteristics of a particular food. However, if only the mechanical properties are considered then good correlation between instrumental and sensory methods may be gained. Mechanical characteristics are those that are manifest by the

reaction of food to stress and include, hardness (firmness), cohesiveness, viscosity, elasticity (springiness) and adhesiveness (Szczesniak, 1963).

2.3 Muscle Protein Gels

Gels are multicomponent colloidal systems that exhibit certain mechanical properties of a solid. The dispersed component and the dispersion medium are continuously distributed throughout the system (Flory, 1974). Another definition more pertinent to the present discussion is "a polymer-solvent system in which there exists a spatial network of fairly stable non-fluctuating bonds (i.e. those which are not destroyed by thermal motion)" (Bezrukov, 1979). Thus a gel is made up of chains of polymer molecules crosslinked at nodes of interaction to form a continuous network structure with the dispersed solvent interacting with the polymer molecules.

A limited polymer solubility is considered necessary for the gelatinous state. Some sections of the polymer molecule adhere to each other forming nodes of interaction, while others remain in solution. Such behaviour is due to the hydrophilic and hydrphobic nature of the polymer molecule. The nodes of interaction are formed as a result of the hydrophobic sections coming into contact with one another, whereas the solvation of the hydrophilic sections ensures the continuity of the network. The types of interaction can involve all types of physical bond (hydrogen, hydrophobic, covalent, salt linkages and physical entanglements).

Thermal irreversibility of gels can be attributed to covalent interactions between polymer molecules in the three dimensional network. The chemical nature of the polymer and the interaction at the junction will dictate flexibility and strength of interactions. In muscle protein gelation, the polymerization is caused by the unfolding and interactions of proteins. Ferry (1948) described gelation of denatured proteins as a two-stage process, consisting of unfolding followed by association into a gel matrix. Subsequent

research has indicated that many proteins have multiple folding domains. Thus depending on the degree of unfolding prior to association, there would be multiple denatured states available to associate into a gel matrix.

2.4 Rheology of Gels

Gels are viscoelastic in nature, that is, they exhibit the mechanical properties of both solids (elasticity) and liquids (viscosity) when subject to a shear. When the shear stress is large enough and sufficient time is allowed both properties are exhibited at the same time. Measurements made involving small deformations of the sample usually measure the elastic properties of the gel and large deformations measure both the elastic and viscous properties (Muller, 1973).

In a perfectly elastic solid strain responds immediately to stress as shown in Figure 2.1A, but gels take a definite time to respond to an applied stress as shown in Figure 2.1B. Because of this time dependency it has been suggested that the most satisfactory way of describing the ultimate properties of a gel is in terms of a "failure envelope", where a gel is tested at various strain rates and temperatures (Mitchell, 1983).

The viscoelastic behaviour is measured by application of a constant or sinusoidally oscillating stress or strain. With constant stress or strain the results can be expressed in terms of the creep compliance function (constant stress),

$$J(t) = \frac{\text{strain (t)}}{\text{stress}}$$

or the stress relaxation function (constant strain),

$$G(t) = \frac{\text{stress(t)}}{\text{strain}}$$

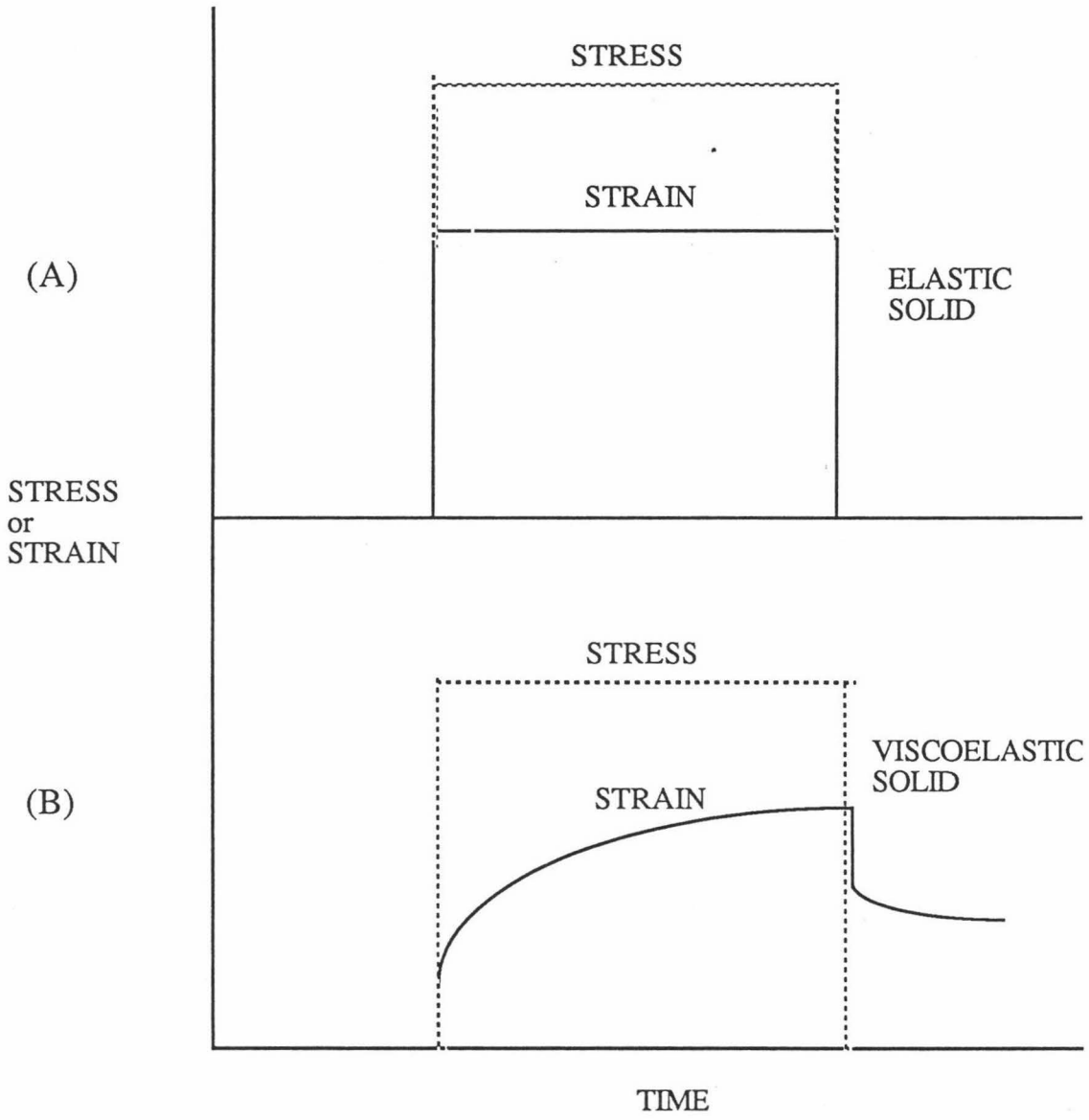

Figure 2.1 The response to a step in the applied stress of;
(A) a perfectly elastic material and
(B) a viscoelastic solid.

Small deformation tests (deformation is well below failure values) can be useful in investigating the changes that occur in food during processing but generally do not relate to structural failure and do not correlate well with texture.

Rheological measurements are made on gels to provide information for use in a variety of applications. Firstly since the gelling behaviour of natural polymers varies with the raw material and the method of extraction, it is essential for both the purchaser and the manufacturer of gelling agents to have a reliable test for evaluating the parameter generally known as the "gel strength". Secondly, rheological measurements can be used to complement the information on the internal structure of a gel obtained from other techniques. In this instance it is desirable to employ fundamental test methods. Thirdly, instrumental measurements may be used in place of sensory methods in the evaluation of the texture of food gels (Mitchell, 1976).

2.5 Structural Failure In Gel Foods

A distinction should be made between a test that ruptures a gel and a method that deforms it without rupture. A series of samples will not necessarily be ranked in the same order of strengths by a rupture and a deformation test (Mitchell, 1976). One of the reasons for this is that the elastic modulus and rupture strength depend in different ways on the primary molecular weight of the polymer from which the gel is formed (Mitchell, 1980)

Consumer assessment of texture involves large deformations of the sample to failure, therefore, rheological measurements of this type are more likely to correlate with perceived texture than the results of experiments involving small deformations. Structural failure means breaking the structural bond between some portion of food and a neighbouring portion on the macroscopic level. Knowing stress and strain conditions causing such breaking are important because they relate to sensory texture.

Relatively little fundamental work has been done on the rupture strength of gels. This is partly because the quantity is difficult to measure reproducibly. Even when measurements are made at a constant rate of strain, rupture strengths are much less reproducible than small deformation parameters because failure takes place at a defect in the sample and the number and extent of such defects varies considerably from sample to sample, (Mitchell,1983).

It has been suggested that the following factors should be considered when evaluating a particular test for use in evaluating gel properties, Mitchell (1980) :

1. The time scale over which the measurement is made,
2. The extent to which the gel is deformed and,
3. Whether or not the gel is ruptured during the test.

2.6 Rheological Methods

Instrumental methods for texture measurement have been divided into three classes, fundamental, empirical and imitative, Mitchell (1976) .

Fundamental tests measure well defined fundamental rheological properties of the material under study. The results are independent of the instrument geometry, sample geometry, and the stress-strain conditions. The results can be confirmed using different sample and instrument geometries thus proving that they are not an artefact of the test itself.

In a fundamental rheological test the stresses and strains of interest in the material must be known. This is only the case for well-defined geometries and loading. Generally, what is measured is a force or torque and a linear or angular deformation. The force/deformation ratio is converted into a stress/strain ratio

by using an appropriate form factor. The form factor will normally have been calculated for linear behaviour. Inertia of the sample is also neglected, although this can be important for some dynamic experiments involving high frequencies.

These tests give numerical data in fundamental units which can be analysed in a systematic manner yielding insights into how physical and chemical structure and chemical composition of foods affects their rheological properties and thus their texture. Theories of the structure of materials, such as the theory of rubber elasticity (Treloar, 1975), make predictions in terms of fundamental rheological parameters; thus, if information about the internal structure of the material is required, fundamental measurements are to be preferred, particularly because in a fundamental test it is known exactly how the sample is deformed. The results can also be used in engineering applications such as equipment design.

Empirical tests measure parameters which cannot be explained in terms of fundamental rheological quantities and, therefore, the results obtained will depend on the geometry of the sample and instrument employed. The conditions of stress and strain existing in the sample are not known and the results cannot be expressed in terms of well-defined rheological parameters such as viscosity and elastic moduli. Furthermore, the results of empirical tests can easily be misinterpreted due to a lack of understanding of what is happening during testing.

Empirical tests have the advantage that they are often easy to perform because any convenient sample geometry can be used. It is only necessary that the method gives both reproducible results and the information required which in the case of gels is an indication of how the gels would be regarded organoleptically. The equipment used is often inexpensive and the tests can be performed easily and rapidly. Empirical tests are the most widely used type of large deformation test used in the food industry. The

instruments used cover a wide range of tests such as puncture, shear, and extrusion.

Imitative tests are empirical tests that measure various properties under test conditions similar to those which the material is to be subjected to in practise, once again the results depend on the test conditions used.

2.7 Correlation Of Instrumental Tests With Sensory Methods For Surimi-Based Foods

In Japan, with its long tradition of eating kamaboko products the sensory property of interest is the *ashi* of the product. The meaning of ashi has been poorly defined in the literature. Tanikawa (1985) describes ashi as the elasticity of the cooked product, whereas Sone (1971) describes ashi as the complex mechanical sensations felt during mastication of kamaboko products, such as the elastic feeling on the back teeth and the resistance to cutting of the sample by the front teeth. Other researchers also describe the elastic component of ashi as being the most important factor in the Japanese consumers perception of the quality of kamaboko products, with the fracture properties still being of importance, but less so (Sano et al., 1986; Tsuji, 1984; Suzuki, 1981).

Many studies have been reported that correlate ashi with instrumental methods. Matsumoto and Arai (1952) pushed a spherical probe into a cylindrical test piece and found that the force required to compress and fracture the sample correlated with ashi. This test was later modified by Okada and Yamazaki (1958) and is now the standard instrumental method used in the Japanese surimi industry. The probe is driven into the sample at a constantly increasing force (variable speed) as water is poured into a probe cup. Reported speeds for the probe are much slower than those commonly used in a modern rheometer, which drives the probe at a constant speed (varying the rate of force increase). A range of probe speeds and probe diameters are described in the

literature. The force at break and the depth of penetration are used to describe the gel properties, often these two values are multiplied together to give the "gel strength". The gel strength is the value that is used in the Japanese grading standards.

However, from the previous discussion of ashi it follows that the texture of kamaboko gels is at least a two dimensional attribute and should therefore be described by at least two mechanical parameters. Toda et al. (1971) suggest that for gels these should be "hardness" and "springiness", whereas Lanier et al. (1985) prefer to use the terms firmness (or strength) and cohesiveness to describe the texture of surimi gels. Thus expression of gel strength as the product of these two variables obscures the relative contribution of each to gel texture. It would also be possible to have the same gel strength score for two samples with one being soft and cohesive and the other firm and brittle.

A number of other instrumental tests have been correlated to ashi, Shimizu (1981) made a ring out of a kamaboko slice by using a smaller diameter "cookie-cutter" technique, which when he then stretched between two hooks until failure occurred. A value calculated from the force and distance of stretch measured at failure correlated well with sensory ashi as determined by a panel.

The texturometer, a compression device originally developed by General Foods or a modified version of this test (Bourne, 1978) has also been successfully applied to the measurement of texture in cooked surimi gels (Lanier et al., 1982; Takagi and Watanabe, 1973) The test is an imitative test, in that it simulates the biting of food in the mouth. Toda et al. (1971) conducted a comparison of the Okada gelometer with this latter technique and found a good correlation between both techniques and with sensory testing. This contrasts with the study by Lanier et al. (1985) where this test did not correlate well with a sensory texture panel. This was explained by the greater numbers of strong textured gels that did not fail under the level of deformation used in this test (74%),

whereas the study of Toda et al. (1971) included a higher proportion of gels that would have failed under these conditions.

The torsion test, a fundamental test developed for food products by Diehl and Hamann (1979) and later modified by Wu et al. (1985) has also shown good correlation with sensory testing. In this test a sample is twisted to failure, the tensile, compression, and shear stresses remain equal at all times, such that the sample will fail due to the mode of stress to which it is least resistant. It is reported that within a wide range of sample properties there is no volume change in the sample during the test. Such a volume change in the sample is common with other tests, and complicates a mathematically accurate calculation of stress and strain.

The torsion test parameter of true shear strain at failure has been shown to correlate with the textural attributes of a wide range of protein gels described by a trained texture profile panel (Montejano et. al., 1985).

Lanier et al. (1985) conducted an extensive study to correlate the punch test, the General Foods instrumental texture profile analysis (ITPA) and the torsion test with a texture profile (sensory) panel. The four sensory attributes used in this study were the rigidity (the force required to slightly compress the sample between the fingers), firmness (the force required to bite through the sample), cohesiveness (the tendency of the product to breakdown during chewing), and gel strength at 5 chews.

They concluded that the torsion test gave the highest correlations with the sensory attributes. Torsional stress to failure correlated best with sensory firmness, and torsional strain correlated best with sensory cohesiveness and gel strength at 5 chews (both are measures of the tendency of the product to breakdown during chewing). The puncture test showed a similar pattern but gave lower correlation coefficients with the sensory panel. The ITPA parameters, as previously discussed, did not show good correlation with sensory attributes. Further analysis showed that

there was a good correlation between the puncture and torsion test parameters, for most gels, and one could be used to predict the other.

The authors then went on to recommend that the torsion method be adopted for use in the USA surimi industry for the determination of texture-forming ability. They reported that the the torsion test had the following advantages over the puncture test;

- better taste panel correlation,
- direct measurement of shear stress and strain at failure,
- greater accuracy with strong gels, and
- less error when testing high moisture gels

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3. DEVELOPMENT OF RHEOLOGICAL METHODS

3.1 Torsion Test

For the torsion test used herein a pure shear state is obtained by applying a twisting moment about a central axis (Diehl et al.,1979; Hamann, 1983) . Undesirable stress concentrations at the locations where the twisting moments are applied are minimized by reducing the cross-section as shown in Figure 3.1. Under these conditions the maximum shear stress magnitude (labelled S in Figure 3.1A) is equal to the maximum normal stress magnitude (labelled T in Figure 3.1A). The shear stress and normal stress act on planes oriented 45° from each other.

The equations for calculating the maximum shear stress, maximum shear strain and true normal strain at failure are described by Diehl et al. (1979) and Hamann (1983). For gels where the slope of the relationship between angle-of-twist and torque is constant at the occurrence of failure, the equation for maximum shear stress is:

$$T_{max} = \frac{3KM_t}{2\pi r_{min}^3} \qquad (1)$$

where

r_{min} = the radius at the smallest cross-section
M_t = the twisting moment (torque)
K = a geometric correction factor correcting for the fact that the specimen is not a cylinder.

It is calculated from the following equation

$$K = \frac{3\left(1 + \sqrt{\frac{r_{min}}{r_c} + 1}\right)^2}{4\left(1 + 2\sqrt{\frac{r_{min}}{r_c} + 1}\right)} \qquad (2)$$

r_c = the radius of curvature at r_{min}

The maximum shear strain is given by:

$$S_{max} = \frac{2K\Psi_t}{\pi r^3_{min} Q} \qquad (3)$$

where Ψ_t = angle of twist in radians, and

Q = a constant based on the geometry of the specimen which proportions the angle of twist as a function of cross-section radius at each increment of specimen length

$$Q = \frac{4}{\pi} \int_0^{z0} \frac{dz}{\left(a - \sqrt{r_c^2 - z^2}\right)^4} \qquad (4)$$

For an instrument that drives the spindle through an internal spring the angle of twist is:

$$\Psi_t = (\Psi_{total} - \Psi_{spring}) \frac{Q}{U + Q} \qquad (5)$$

When the specimen is twisted by applying a moment to the end view sections the rotation in the end sections is given by:

$$Q_{ends} = U = \frac{32L}{\pi D_e^4} \tag{6}$$

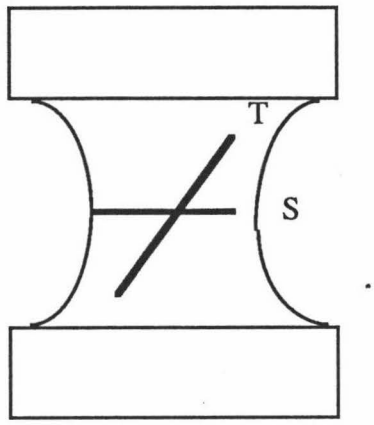
where

L = sum of the length of the two end sections
D_e = diameter of the end sections

The true normal strain is given by,

$$S_{true} = \frac{1}{2} \ln \left[1 + \frac{S_{max}^2}{2} + S \sqrt{1 + \frac{S_{max}^2}{4}} \right] \tag{7}$$

(A)



(B)

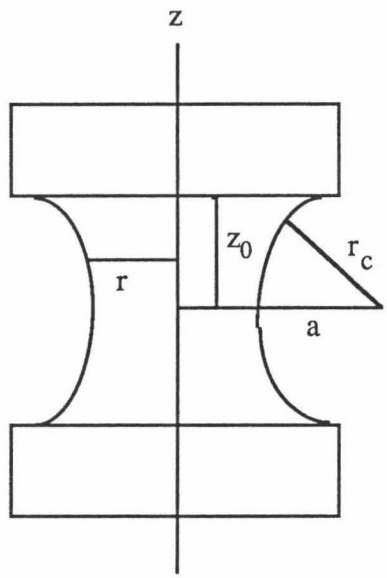


Figure 3.1 (A) Planes of maximum shear and tensile stress in a rod in torsion

(B) Critical dimensions of dumbbell shape used for torsion tests (from Diehl et al., 1979)

3.1.1 Experimental Method

Teflon disks were attached to 24 mm long gel samples with cyanoacrylate adhesive (Loctite, UK). The samples were then placed in a grinding jig and formed into dumbbell shapes with a range of minimum radii (Figure 3.2). These radii were measured by vernier calipers. The samples were then twisted to failure using a Ferranti Shirley Viscometer by adapting the procedure described by Montejano et al. (1983), Figure 3.3. Shear stress and true strain at failure were calculated using the equations described above.

Figure 3.4 shows a typical output for the chart recorder, note that the slope is constant at the occurrence of failure.

For the samples and grinding wheel the critical dimensions are;

$r_c = 0.0075$ m

r_{min} = various

therefore,

Q = various

$z_0 = 0.0064$ m

$\frac{U}{2}$ section = 0.03 m

therefore,

$U = \frac{32L}{\pi D^4}$ where D = diam. of $\frac{U}{2}$ sections

L = sum of the lengths of the $\frac{U}{2}$ sections = 0.024 m

therefore,

$U = 3.018 \times 10^5$ m^{-3}

see Appendix 1 for a copy of the Minitab program used to manipulate data and a sample program output.

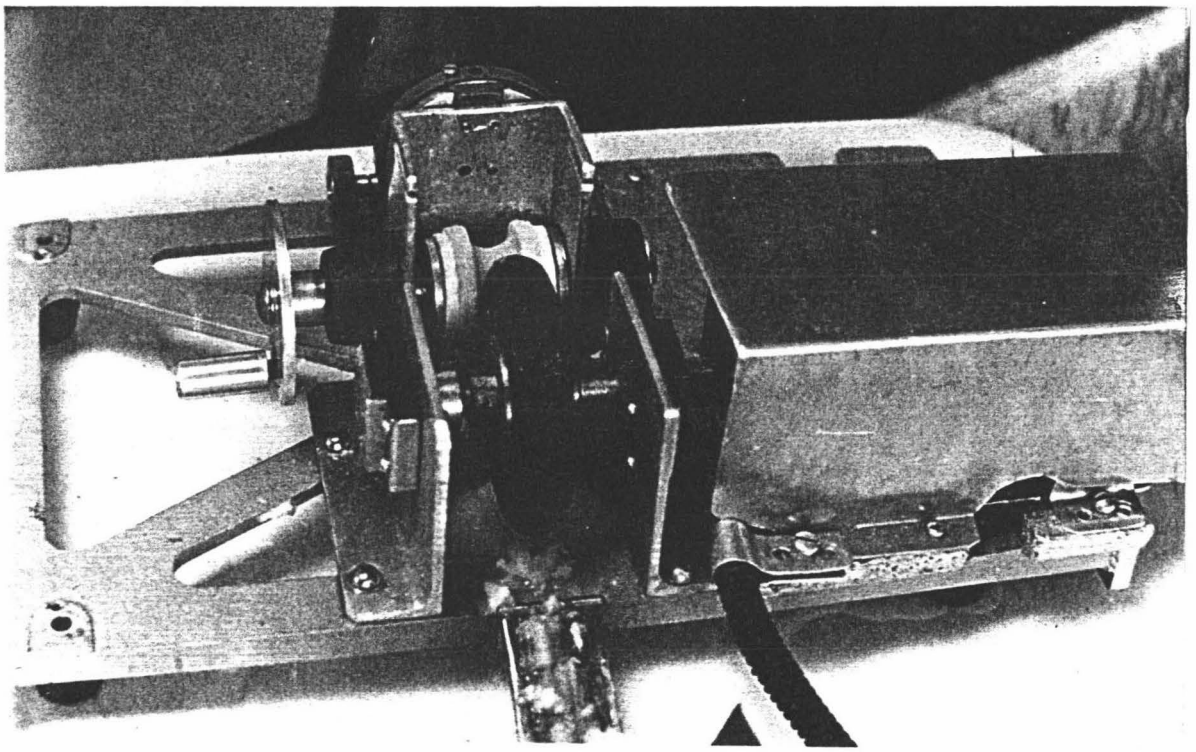


Figure 3.2 Grinding rig for preparing dumbbell shaped samples

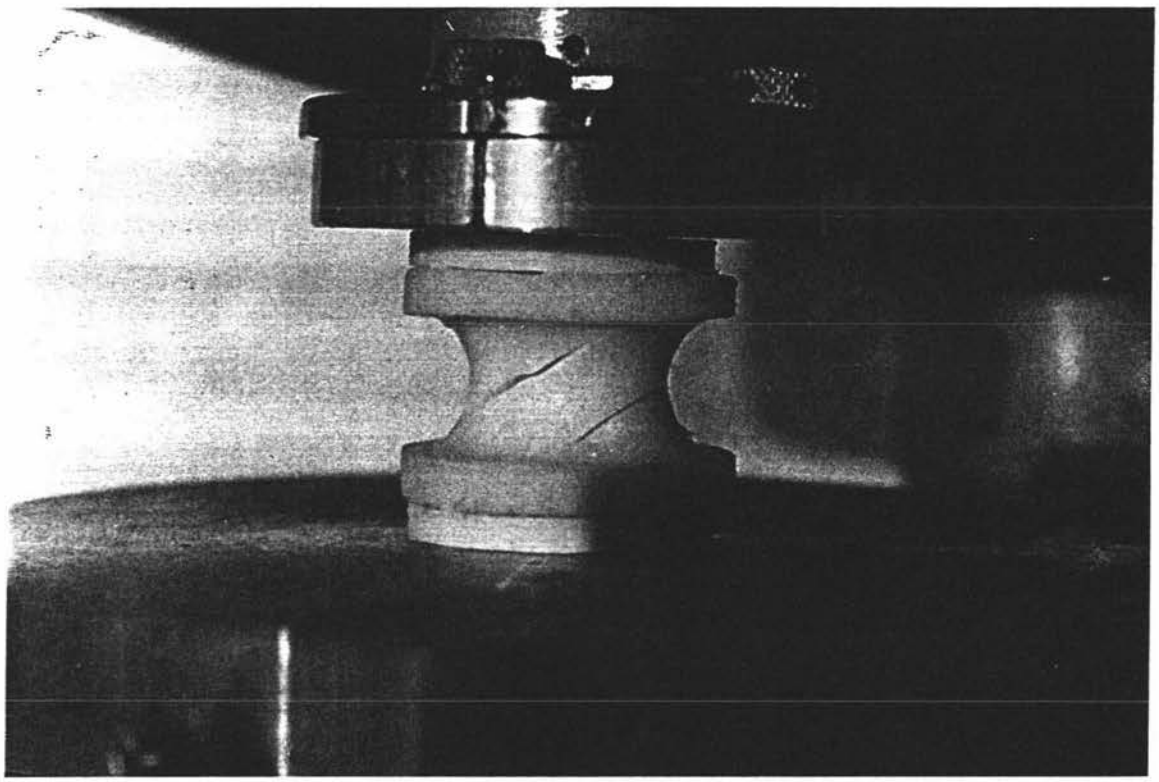


Figure 3.3 Dumbbell shaped sample under test in the Ferranti Shirley Viscometer

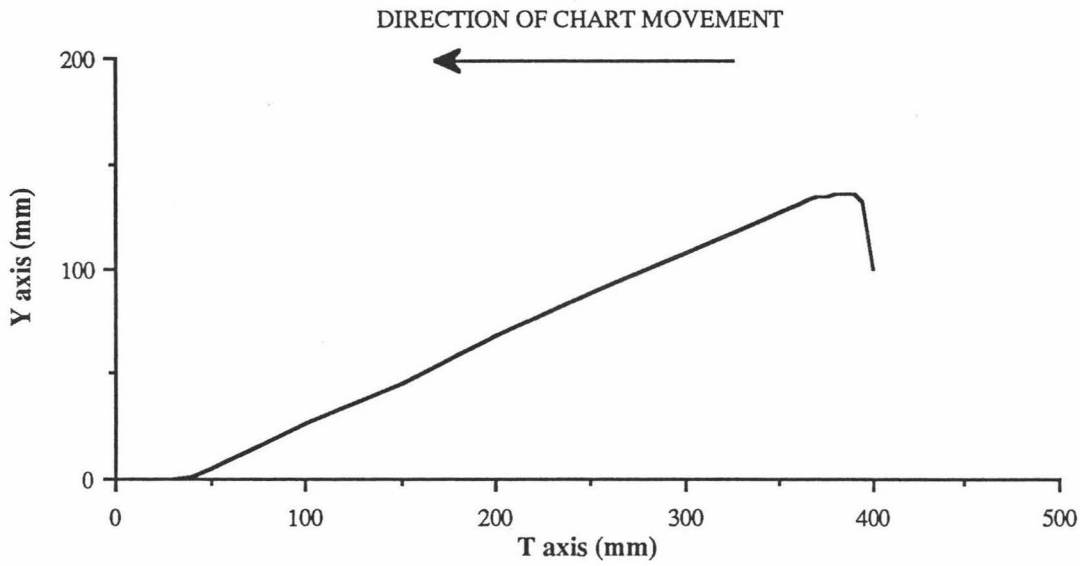


Figure 3.4 Example of a torsion test chart readout

3.1.2 Verification Of Equation (1)

In order to test equation (1) gels were tested at different minimum radii and torque (M) was plotted against (r^3/K). This plot should yield a linear relationship with slope = $(2\pi/3)T_{max}$ from which T_{max} can be evaluated.

Figure 3.5 shows an example of such a plot for a fish gel, the correlation coefficient is significant at the 99% confidence level, thus verifying equation (1).

The shear strain cannot be tested in this manner because it is a function of the radius.

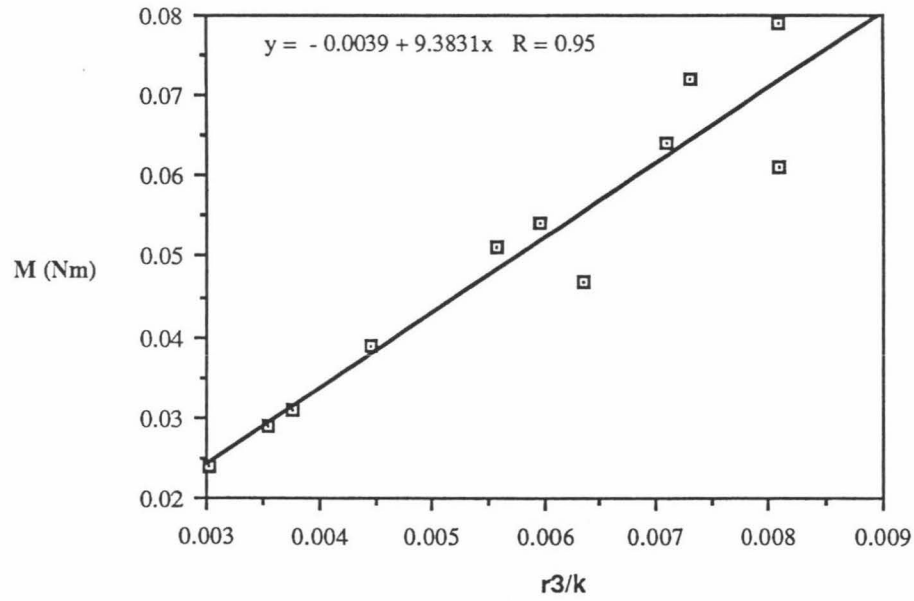


Figure 3.5 Plot of torque (M) against (r^3/K) for different minimum radii.

3.1.3 Effect Of Spindle Speed On Torsion Test Parameters

Fish gels are viscoelastic and the rate at which the gel is deformed during measurement may be important, therefore the effect of various spindle speeds on torsion test parameters was investigated. Gels were made from a medium grade commercial hoki surimi (made at sea) and tested at spindle speeds of 0.25 to 2.0 rpm. The results of these studies are reported in Table 3.1. Over this range of speeds there were no significant changes in either shear stress or true strain at failure. A speed of 0.5 rpm was used for subsequent studies.

Table 3.1 The effect of spindle speed on torsion test results

Spindle Speed (rpm)	Torsion Parameter		
	Shear Stress (kPa)	True Strain	Rigidity (kPa)
0.25	51.1	2.38	22.0
	(1.7)	(0.42)	(4.4)
0.5	50.1	2.27	22.3
	(2.8)	(0.28)	(1.7)
1.0	53.5	2.37	22.7
	(5.1)	(0.11)	(3.0)
1.5	52.1	2.49	21.1
	(6.4)	(0.21)	(3.4)
2.0	57.0	2.42	23.6
	(3.5)	(0.12)	(1.8)

Standard deviations are in brackets

3.1.3 The Effect of Grinding On Gel Properties

Another possible source of variation may occur as a result of stress on the gel during the grinding operation when the gel is rotated by winding a handle fixed to one end. It is possible that this stress may weaken the gels, or that creep, with the breaking and reforming of weak bonds in the gel, may take place during this operation.

The effect the grinding operation may have on the results was tested by orientating ground gels on the Ferranti Shirley with either the handle-end uppermost or positioned on the bottom. With the handle-end up the twisting moment to failure is applied in the same direction as the stress is applied during grinding and with the handle-end down the twisting moment is applied in the opposite direction.

The means and standard deviations of three sets of gels were compared with respect to orientation on the torsion apparatus. However, there was no significant difference ($p < 0.05$) between the treatments for both shear stress or true strain at failure.

3.2 The Puncture Test

Punch penetration of the end of a cylinder 30 mm diam. and 25 mm long is a standard method for testing kamaboko in Japan (Lee, 1984). The punch normally used is a 5 mm diam. sphere driven by a smaller diameter shaft (Figure 3.6). The stress and strain patterns in the gel are unknown for large deformations such as those encountered in gel strength testing.

The values measured in the puncture test are;

1. maximum force at failure, N or gms
2. deformation from the point of contact to failure, cm

and the calculated values are;

3. gel strength = max. force x deformation to failure, gm.cm, N.cm
4. stiffness = max. force / deformation to failure, gm/cm, N/cm

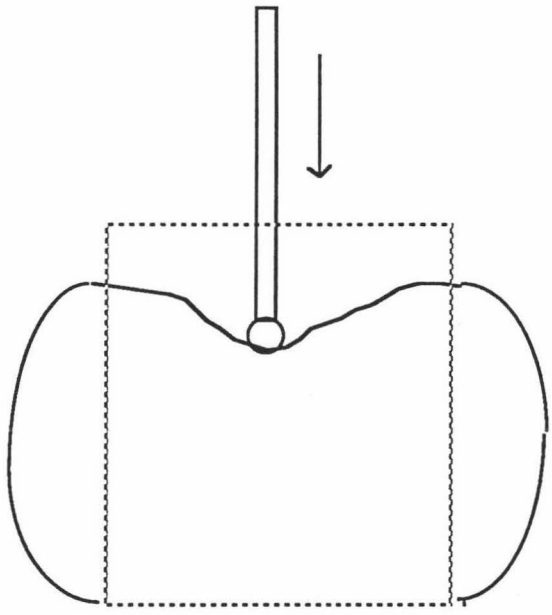


Figure 3.6 Sample shape during the puncture test

3.2.1 The Effect Of Penetration Speed On Puncture Test Parameters

Although an attempt has been made to standardize the puncture test used for surimi testing (Anon., 1984), review of the literature shows that a wide range of probe speeds (10 mm/min to 60 mm/min) have been used when testing surimi. Mitchell (1983) reports that both the stress and strain at rupture will depend on the rate of deformation. However, Kamel and deMan (1977) showed that for gelatin gels the force reading was independent of the speed (24 mm/min to 72 mm/min) for a range of punch shapes and sizes. The effect changes in penetration speed may have on the results from the puncture test when testing surimi gels is unclear.

The effect of probe speed was investigated by making three surimi gels with different textural properties. The two surimis used were SA grade hoki (made at sea) and a lower quality surimi from Thailand (made on-land from *Nemipterus* spp.). Water was added to make a softer gel.

(1) a low moisture gel made with high quality surimi, (firm and cohesive)

(2) high quality surimi with 40% (w/w surimi) water added, (soft and cohesive)

(3) a low moisture gel made with low quality surimi, (firm and brittle)

The gels were tested with a 5 mm diam probe and penetration speeds of 10, 20, 50, 100, and 200 mm/min using a Universal Testing Machine (Instron, model 1000).

The results of this experiment are shown in Figure 3.7. Contrary to the results of Kamel and deMan (1977), as the penetration

speed increased the force at failure value increased significantly. This reason for the difference may be the elastic nature of gelatin (Mitchell, 1980) as compared with the viscoelastic nature of surimi-based gels.

The general trend of the results is consistent with each gel type, however, the gel with the lowest initial force value, the weakest gel (2), showed the smallest changes in force value as penetration speed increased. For the surimi gels tested, a change in penetration speed from 10 mm/min to 50 mm/min, the range of most commonly used speeds, increased the force value by; (1) 19%, (2) 20%, (3) 11% respectively, a significant change.

The results suggest that there is a significant viscous component in surimi gels and a significant amount of creep may take place prior to rupture when the rate of deformation is slow enough. Thus the rate of deformation is an important consideration when selecting a test method.

The deformation at failure did not change greatly with increased penetration speed.

Clearly, there is a need to standardize methodology for testing surimi, and great care should be taken when comparing puncture test results from the literature. For the work described in the following studies a probe speed of 20 mm/min is used as it is the speed recommended for the standard Japanese method (Anon., 1984).

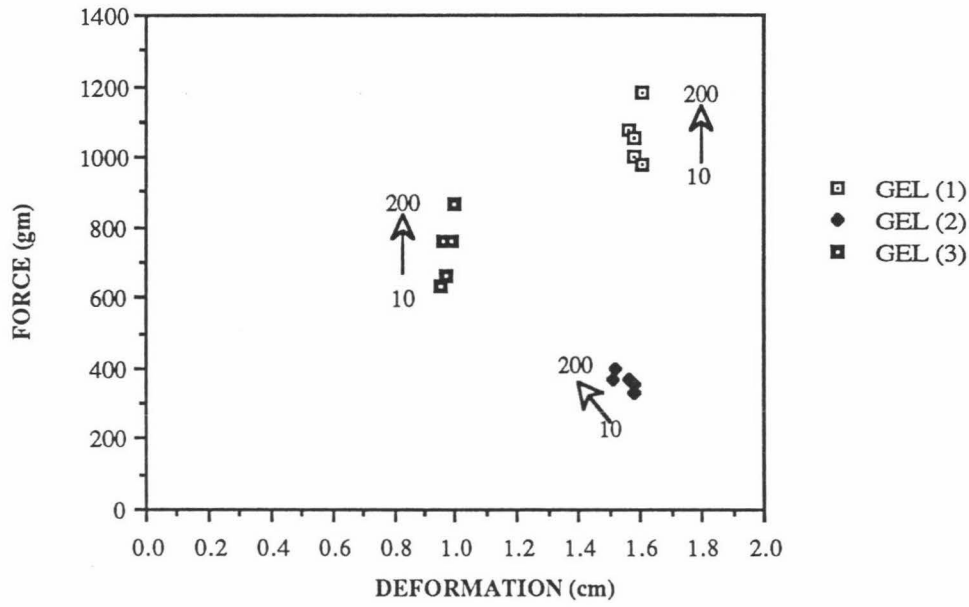


Figure 3.7 Puncture test force and deformation at failure for three gels tested at different probe speeds(10, 20, 50, 100 and 200 mm/min). The arrows show the direction of increase in probe speed.

3.3 References

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4. THE STRENGTH OF GELS MADE FROM WASHED AND UNWASHED MINCE MADE FROM HOKI (*Macruronus novaezelandiae*) STORED IN ICE.

4.1 Introduction

Hoki (*Macruronus novaezelandiae* Hector) is an important commercial fish species in the New Zealand Exclusive Economic Zone. The fish can be processed into high quality surimi (Sonu, 1986; Iwata and Yamada, 1969), that is surimi with the ability to form relatively strong gels. Since significant quantities of hoki can be caught quite close to land, there is interest in manufacturing surimi on-shore. However it is uncertain how such an operation would affect surimi quality because the fish would have to be stored in a chilled condition before processing. Work on other species suggests such storage causes the strength of gels made from surimi to decline (Yasui et al,1987; Haard and Warren, 1985; Noguchi, 1982; Kurokawa, 1979).

The objective of the present study was to investigate the strength of gels formed at 60 and 90°C from washed and unwashed minces prepared from hoki stored in ice for various times. Washed minces are a model for the more complex surimi system while unwashed minces act as a control (Noguchi,1982; Kudo et al.,1973) and allow the influence of sarcoplasmic proteins and alkaline proteases to be studied. The use of a gel formation temperature of 60°C, as well as the 90°C normally used by the Japanese industry (Shimizu,1981; Suzuki,1981), provides a further means of studying the effect of alkaline proteases since these enzymes degrade gels at 60°C (Lanier, 1984; Su et al,1981; Lanier et al,1981; Lin and Lanier,1980).

Many methods of measuring gel strength are available and the puncture, folding, and torsion tests were used in the present study because the first two of these are of significance to the Japanese market while the third test has been proposed as a reference method in the United States. A sensory panel was also

used to describe the texture of the gels. The condition of the hoki in ice was monitored by a trained sensory panel, pH measurement and nucleotide analysis.

4.2 Materials And Methods

4.2.1 Fish Capture, Storage and Proximate Analysis

Hoki were caught on 3 August 1986 at a depth of 470-500m in area G (Lat,41°S, Long,170°E) by bottom trawling. The trawl time was approximately 2 hrs 30 min and the water temperature at 500m depth was 8.5°C. The fish were immediately removed from the deck and placed in ice. Upon arrival at the laboratory 18 hrs later, the fish and ice were transferred to an insulated container. The ice was completely replaced at day 8 of the trial.The protein, ash, oil and moisture contents, length and weight of 6 one day old fish were determined according to Vlieg (1984).

4.2.2 Preparation of Fish for Freshness Assessment and Mince Manufacture

Fish were assessed on arrival at the laboratory and every 2-3 days thereafter. On each occasion, sections of white muscle were removed from the anterio-dorsal region of 5 fish for sensory assessment after cooking, flesh pH measurement, and nucleotide analysis. These fish, together with 5 others were then filleted, and the fillets were trimmed to remove the black belly lining (peritoneum) ready for mince manufacture.

4.2.3 Measurement of Fish Freshness

Sensory assessment. The organoleptic quality of the fish were assessed at each sample time by a panel of three judges experienced in fish quality assessment. The attributes of general appearance, gill odour, flesh and gut cavity appearance, raw

texture, cooked odour, cooked texture, and cooked flavour as described by Baines and Shewan (1965) were used.

Muscle pH. The muscle pH was determined using 0.01 M neutral sodium iodoacetate as described by Boyd et al (1984).

K value. Adenosine 5' - triphosphate (ATP) and its breakdown products were measured, in perchloric acid extracts of muscle, by ion exchange chromatography using the method of Ehira and Uchiyama (1976). The K value, calculated as the ratio of the sum of hypoxanthine and inosine to the total amount of ATP related compounds, was determined according to Saito et al (1959).

4.2.4 Preparation of Fish Minces

Immediately following filleting and trimming, the fillets were passed through a Bibun (Model NF2DX) meat separator fitted with a screen with 4 mm holes. The resulting mince was divided into two portions. One portion (2kg) was sealed in a polythene bag and chilled forl hr in ice prior to being made into a gel. The other portion (3 kg) was washed 3 times in 5 volumes of ice water with 0.1% NaCl added to the last wash to facilitate dewatering. Each wash consisted of stirring the mince with the water for 60 sec followed by holding for 10 min to allow the mince to settle, after which the supernatant was decanted and the mince was drained through a muslin bag. After the third wash the mince was dewatered in a basket centrifuge lined with muslin. Centrifuging was continued for 5 min after most of the fluid had stopped flowing from the mince. The moisture content of the washed mince was adjusted to approximately 80%. A 2 kg portion of the washed mince was then sealed in a polythene bag and chilled in ice for 1 hr prior to making gels.

4.2.5 Preparation of Gels

Gels were prepared either by chopping the unwashed or washed mince in a prechilled Hobart silent cutter (Model 8145, Hobart

Corp., USA). 2.5% (w/w) NaCl and 0.2% (w/w) phosphates (50:50 blend of sodium tripolyphosphate and sodium pyrophosphate) were added after 1 min of chopping. The total comminution time was 6 min. The final temperature of the resultant paste was always less than 12°C. The paste was then placed in a hydraulic sausage stuffer (Gillespie, Auckland, N.Z.), and filled into 48 mm folded width polyvinylidene chloride casings (Kureha, Japan) to form sausages 30 cm long with a diameter of 30 mm. The casings were filled to approximately the same pressure prior to sealing. The sausages were then divided into two batches, one batch was cooked at 60°C for 40 min and the other at 90°C for 40 min. (representative heat penetration curves are presented in Appendix 2). After cooking, the gels were chilled in an ice water slurry and held at 4°C. This gave 4 gel samples in total which were labelled as follows: U60, unwashed/60°C; U90, unwashed/90°C; W60, washed/60°C; W90, washed/90°C.

4.2.6 Assessment of Gels

Gels were equilibrated at 20°C for1 hr before testing. All tests were carried out within 48 hr of gel preparation. A check was made to confirm that gel properties did not change on storage at 4°C.

Moisture content. The moisture content of the gels was determined by drying in an air oven at 105°C for 18 hrs.

Puncture test. The gel strength was determined according to Shimizu (1981) using a Universal Testing Machine (Model 1122, Instron). A sample of length 25 mm was cut from the heat-processed gel and tested using a 5 mm spherical probe with a crosshead speed of 20 mm/min. When the surface of the specimen was broken, as detected by the rapid fall in the force value, the force (N) and the deformation (cm) were measured. The gel was then turned over and the test was repeated on the opposite end. There was no significant difference ($P<0.01$)

between the means of determinations from both ends of the same sample. The results of 16 determinations were averaged. The puncture gel strength was calculated as the force multiplied by deformation at failure (Suzuki, 1981; Shimizu et al, 1981).

Torsion test. Teflon disks were attached to 24 mm long gel samples with cyanoacrylate adhesive (Loctite, U.K.). The samples were then placed in a grinding jig and formed into dumb-bell shapes with a range of minimum radii. The radii were measured by vernier calipers. The sample was tested to failure in the torsional mode by adapting the procedure described by Montejano et al. (1983) to a Ferranti Shirley Viscometer. The samples were twisted at 0.5 rpm to failure as described by M^{c}Carthy (1987). Shear stress and true shear strain at failure were calculated using the equations developed by Diehl et al. (1979). Eight determinations were made and the results averaged.

Folding test. The folding test for elasticity was performed by folding a 3mm thick by 30 mm diam. slice of the gel into quarters. The more a slice could be folded without cracking the more elastic the gel. The average of five determinations using the 5 point numerical scores of Shimizu (1981) was found.

Sensory texture evaluation. The sensory texture score was determined by at least three experienced panelists using the10 point score method of Shimizu (1981) and results were averaged.

4.2.7 Statistical analyses

Analysis of variance and student's t-test were employed to evaluate data for the significance of the degree of variation and the difference between treatments using Minitab (Ryan et al, 1982).

4.3 Results And Discussion

4.3.1 Initial Characteristics of the Hoki

All the fish contained mature gonads and started going into rigor about 40 min after landing. Rigor was resolved after about two days storage in ice. The proximate analyses and physical characteristics of the day old fish are given in Table 4.1, the length and weight of the fish are consistent for spawning hoki from the same grounds in other years (Patchell,1982).

Table 4.1. Composition of Hoki Flesh.

	Mean	Standard Deviation
Length (cm)	76	9
Weight (g)	1382	35
Sex	3 Female 3 Male	
Protein (%W/W)	15.8	0.7
Oil (%W/W)	1.8	0.8
Ash (%W/W)	1.0	0.1
Moisture (%W/W)	81.3	1.3

4.3.2 Changes in Hoki on Storage

There was a significant change ($P< 0.05$) in muscle pH on day 2 as shown in Figure 4.1, which coincided with the resolution of rigor. Another significant increase ($P<0.05$) occurred after 21 days storage in ice, presumably due to bacterial spoilage of the flesh. The concomitant increase in K value was almost linear with storage time ($r^2 = 0.82$, $P<0.01$), see Figure 4.1. The observations of the sensory panel suggested three stages of spoilage which corresponded to K values of less than approximately 20%, between 20 and 40% and greater than about 40%. Up to a K value of 20% the fish was considered by the panel to be of high organoleptic quality, this is in agreement with other species (Ehira, 1976). Once the K value reached about 40% strong off-flavours and odours, of the type expected from microbial spoilage, were apparent. (The full taste panel results are presented in Appendix 3).

4.3.3 Changes In Gel Properties With Fish Spoilage

Gels could not be made from washed minces on day 1 and day 2 when the fish were in rigor due to excessive disintegration of the muscle fibres during washing and the consequent loss of tissue at the dewatering stage. However, from day 4 it was possible to prepare washed minces. There was a slight variation in moisture content of the gels, from one hoki mince to the other, and this would be expected to have an influence on their rheological properties. However there was no systematic variation in moisture that could account for the observed changes in rheological properties over time.

Puncture Test. All treatments gave a significant decrease in both the puncture deformation at failure and the gel strength with storage of the hoki in ice (Figures 4.2 and 4.3). Some data is missing on day 1 and day 15 because equipment was not available. The lower initial gel strength and puncture deformation of the samples set at 90°C as compared to the corresponding gels

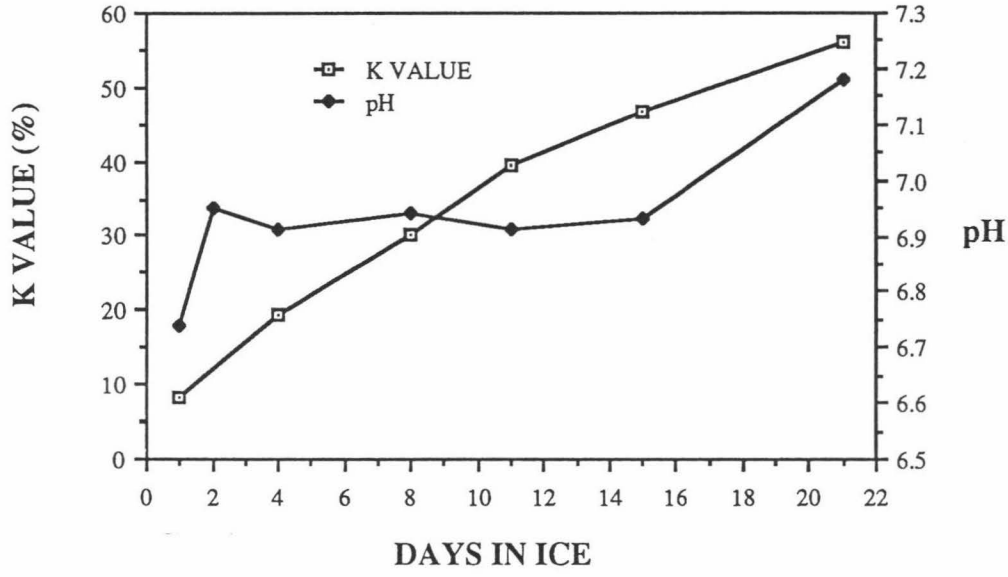

Figure 4.1 Changes in muscle pH and K value of hoki stored in ice

and could be due to the precipitation of sarcoplasmic proteins onto gel formation sites on the myofibrillar protein prior to gel formation (Suzuki, 1981). The slower heating to 60°C allows ordering of the gelling proteins, an integral part of gel formation, prior to denaturation of the sarcoplasmic proteins (Suzuki ,1981). The strength and puncture deformation of the gels made from washed mince were generally greater than those made from the corresponding unwashed minces. This difference was consistent with the results of Sadowska and Sikorski (1976) who found that on the removal of fish albumins the gel strength increased by 30%. In the later stages of the trial the gels made from unwashed mince at 60°C underwent textural deterioration as evidenced by the relatively large decline in the puncture deformation. This indicated the presence of heat stable alkaline proteases. The protease enzymes possibly originated from the gut (Lanier,1986).

Torsion Test. There was a significant increase in shear stress at failure of the gels made from unwashed mince from post-rigor hoki compared to gels from hoki in rigor, see Figure 4.4. This contrasts with Alaska pollock which has been reported to loose half its gel forming ability while passing through rigor (Shimizu, 1985). However once rigor was resolved the shear stress at failure values for all treatments showed a significant decrease with ice storage of the hoki (Figure 4.4). There is no torsion data for sample W60 on day 4 because of unusual failure of the gel casings during heating.

Previous work has shown that the torsion strain measurement is a good indicator of the functional quality of the proteins involved in gelation (Lanier, 1986). In the present investigation true shear strain values showed a significant overall decline for all treatments, Figure 4.5. This is similar to the deformation values from the puncture test. However, there was increased scatter in the results compared to the puncture test, possibly due to the greater sensitivity of the torsion test to the incorporation of air in the gels. This occurred during chopping and was especially evident when making gels from washed mince.

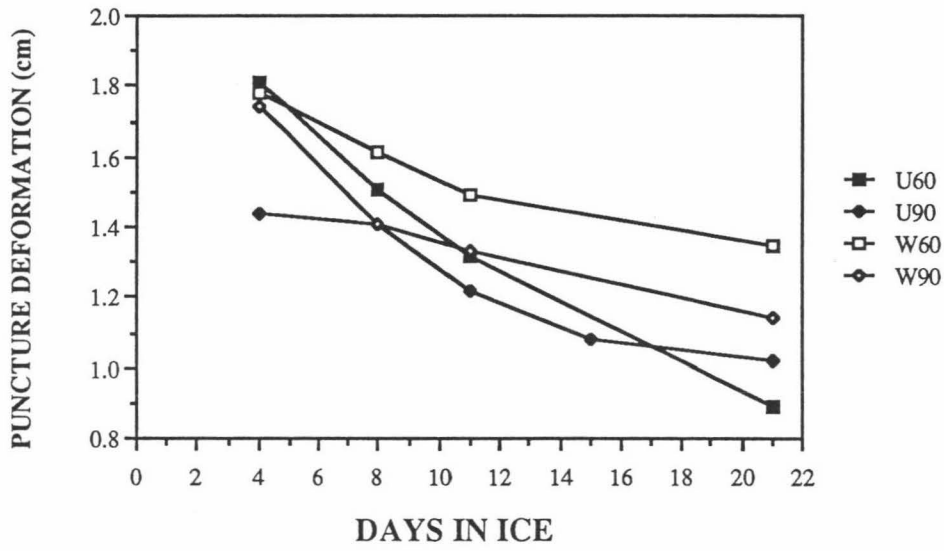

Figure 4.2 Changes in puncture deformation of gels made from hoki stored in ice

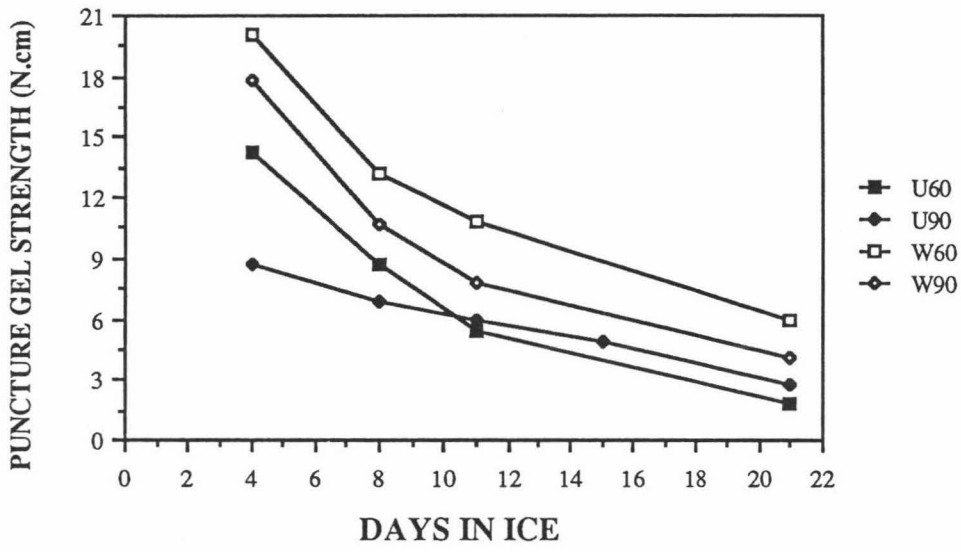

Figure 4.3 Changes in puncture strength of gels made from hoki stored in ice

The shear stress values at failure for washed gels are all higher than those for gels made from unwashed mince, which is consistent with the puncture test. However the unwashed gels set at 60°C showed lower shear stress values than the corresponding gels heated at 90°C while the washed gels showed little difference until the end of the trial. This is in contrast to the puncture test. Similarly to the puncture test, true strain at failure values for gels made from washed minces were higher than those from unwashed minces. No trends were seen in the true strain at failure with respect to gel heating temperature until day 21 when the 60°C gels were lower than the 90°C gels. The shear stress values for gels from washed minces in the present study are higher than the figures reported by Kim et al. (1986) for surimi-based gels made from sea trout and Alaska pollock cooked at 90°C, of 28kPa and 36 kPa respectively.

Sensory texture score and folding test. There was an increase in sensory texture score of the U60 sample at day 4 compared to the sample made from in-rigor fish. This pattern was similar to that from the shear stress measurements. However, an increase was not evident in the U90 sample (Figure 4.5). Once rigor was resolved the sensory texture scores for all treatments showed a decrease over the time of the trial (see Figure 4.6). The U90, W60 and W90 gels showed no change in folding test score throughout the trial with scores of 5. However the U60 sample declined from 5 at day 11 to 2 at day 21, showing the effects of proteases on the gel texture. Clearly the folding test is not sensitive to differences between gels made from reasonably good quality fish.

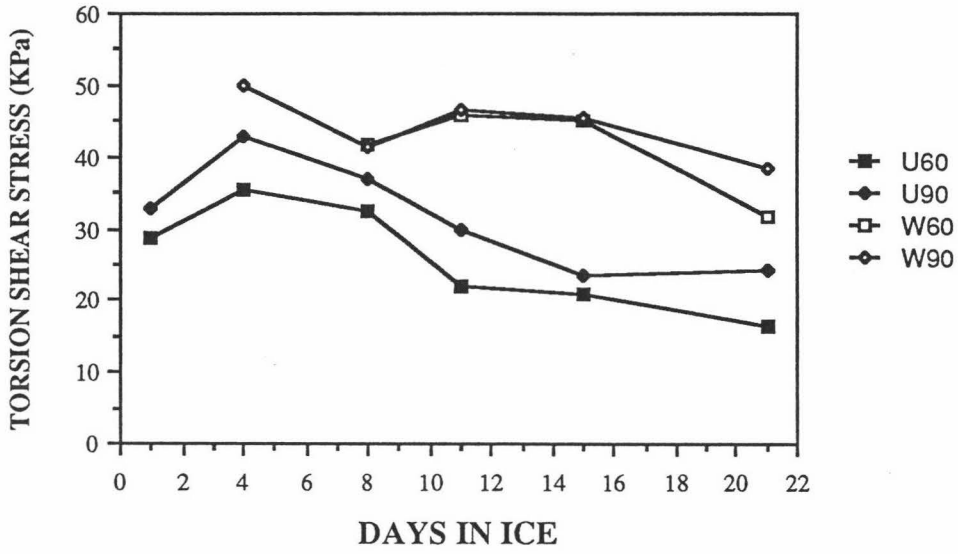

Figure 4.4 Changes in torsion shear stress of gels made from hoki stored in ice

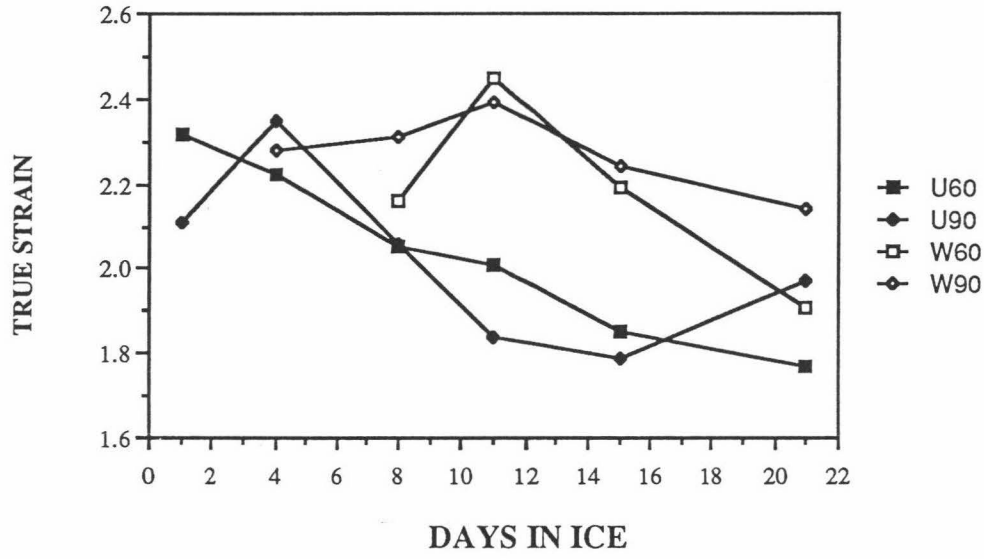

Figure 4.5 Changes in torsion true strain of gels made from hoki stored in ice

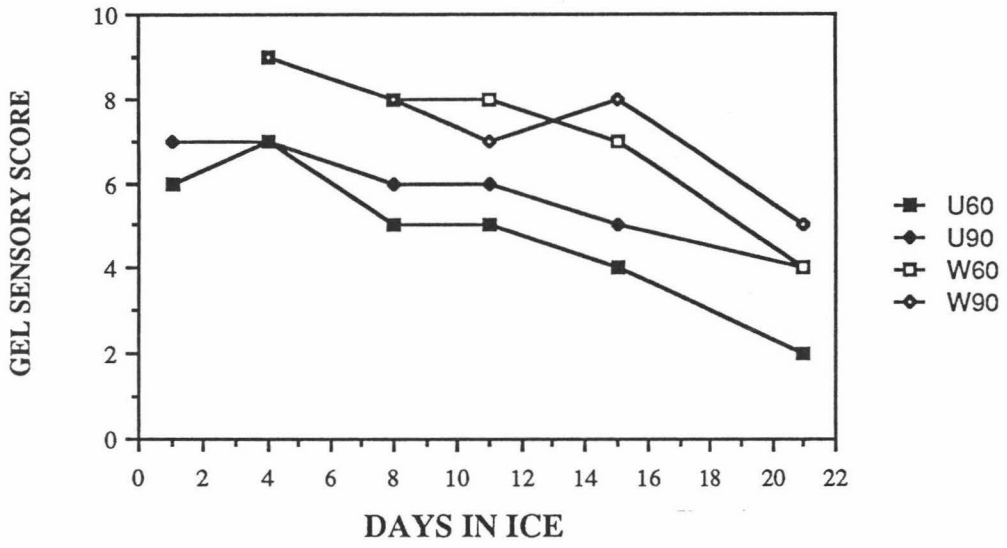

Figure 4.6 Changes in sensory texture score of gels made from hoki stored in ice

4.4 Implications for an On-shore Operation

The present study suggests that surimi made from fish immediately after rigor, as may occur in a factory ship operation, is potentially of the best quality. The strength of gels made from such surimi would be expected to be high on the basis of the W90 gels and this is consistent with previous work which reported that hoki has very good gelling qualities (Okada, 1978; Iwata and Yamada, 1969). Thereafter a loss in gel strength was found as the fish spoiled. The decline in gel strength for hoki was slower than that described for lizard fish for which there was a 50% decline after 3 days storage in ice (Kurokawa, 1979). The decline for hoki also appears to be slower than for Alaska pollock for which it is generally accepted gives only a second grade product after 3-4 days storage in ice (AFDF Project Summary, 1987; Lee, 1986; Okada, 1978). However even after 10 days storage, the gel strength was such that hoki would still have excellent gelling properties according to the classification systems based on Alaska pollock of Okada (1978) and Iwata and Yamada (1969). The shear stress at failure of the W90 gels at this stage compares favourably with the values for Alaska pollock and sea trout surimi gels reported by Kim et al (1986). Hence given that fish from vessels with chilled storage are likely to be less than 10 days old at landing, all the hoki would be expected to be useful for surimi manufacture if stored correctly. However to make a consistent product, an on-shore operation would require strict control of fish quality. Measurements of fish freshness based on organoleptic assessment and the K value may be a useful basis for a hoki surimi quality assurance program.

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5. EFFECT OF FROZEN STORAGE ON THE CHEMICAL AND GEL-FORMING PROPERTIES OF HOKI (*Macruronus novaezelandiae*))

5.1 Introduction

There is interest in utilising frozen hoki for the production of surimi. This is because most hoki is caught in a relatively short period each year (July-August) and the use of frozen hoki would increase production flexibility and could allow a land-based surimi operation to be operated year round. Greater utilization of the surimi plant would also improve the economics of producing surimi on land provided storage costs are not excessive. Furthermore, New Zealand currently has available considerable capacity for heading, gutting and freezing fish at sea and processing on-shore could provide a lower cost alternative to developing a fleet of at-sea surimi processing vessels.

Another feature of on-shore production is that food products could be made directly from solubilised myosin without going through surimi manufacture, this would obviate the need for cryoprotectants and so allow the production of less sweet finished products.

Attempts to utilize other species of frozen fish for the production of surimi-based products have been unsuccessful. Alaska pollock has been shown to be very unstable to freezing and frozen storage and looses its gel forming ability quickly (Scott et al, 1988). Lizard fish stored for two weeks at -27°C had only 50-60% of its gel-forming ability remaining when compared to fresh fish (Kurokawa, 1979). Jiang et al. (1985) investigated the effect of different storage forms of mackerel and amber fish on gel-forming ability, protein quality and water holding capacity and concluded that gutted, headed and gutted and fillet samples showed most stability during three months storage at -20°C. Holmquist et al. (1984) concluded that red hake fillets stored at -8°C for two weeks were no longer suitable for making kamaboko.

The loss of protein functionality and, in particular, the gel-forming ability in frozen fish is due to freeze denaturation and aggregation of the myofibrillar protein (Grabowska and Sikorski, 1976; Sikorski et al, 1976; Matsumoto, 1980; Suzuki, 1981).

Hoki has similar processing and storage characteristics to its close relative the merluccid hakes (Bremner, 1980). Hoki produces dimethylamine and formaldehyde (FA) from the enzymic breakdown of trimethylamine oxide (TMAO) during frozen storage. The FA reacts with myofibrillar protein forming intramolecular and intermolecular crosslinks resulting in a toughening of the flesh and a loss of functional properties (Sikorski et al, 1976; Matsumoto, 1980).

The purpose of this section of this study was to examine the gel-forming ability of hoki stored frozen in a headed and gutted form at -29°C for up to 260 days. The gel-forming ability was determined by rheological tests on gels made from washed and unwashed minces and these were correlated with raw material quality as determined by chemical tests.

5.2 Materials and Methods

5.2.1 Fish Processing and Storage

Hoki as described in Section 4 (Effect of Chilled Storage) were processed after two days storage in ice. The heads, guts and tails were removed and the fish were then blast frozen in 10 kg blocks overnight at -30°C. The blocks were then packed into high density polybags and waxed cardboard cartons and then stored at -29 ±2°C until sampled.

5.2.2 Preparation of Fish for Freshness Assessment and Mince Manufacture

Fish were assessed after 1, 3, 6 and 9 months storage. On each occasion, a 10kg block of fish was thawed in cold running water for two hours until the H&G trunks were able to be filleted by hand. Thereafter preparation of the minces and gels was as previously described in Section 4. .

5.2.3 Measurement of Fish Freshness

Muscle pH and K value were determined as described previously (Section 4). The K value determination was carried out to keep a check on the quality of hoki used in the study. For the processing conditions described the K value should be less then 20% (equivalent to 4 days in ice), and would not be expected to increase on frozen storage.

Preparation of fish mince and gels and assessment of the gels was carried out as previously described.

Flesh moisture was determined by drying 8-10g minced flesh in an air oven at 105°C for 18 hrs.

Expressible moisture Expressible moisture of the flesh was measured by centrifuging 1-2g finely chopped flesh wrapped in no.2 Whatman filter paper for 30 min. at 2500xG. The expressible moisture was calculated as the weight increase of the filter paper as a percentage of the original flesh weight.

Formaldehyde concentration An extract was prepared from thawed flesh according to the method of Mackie and Thomson (1974). 20g minced fish were weighed and placed in a Waring blender (MSE) with 60 ml 0.6 M perchloric acid and comminuted for 2 min. The extract was filtered by aid of vacuum, through a No.1 Whatman filter and left in the refrigerator for several hours, then filtered again through No.1 Whatman filter paper. The

estimation was carried out according to the method of Nash (1953); to 2 ml of extract another 2 ml of reagent containing 2 M ammonium acetate, 0.05 M acetic acid and 0.02 M acetylacetone was added and mixed vigorously by hand. The mixture was then placed in a 60°C water bath for 5 min., cooled in cold water and read at 412 nm on a spectrophotometer (Hitachi, model 100-20); 0.6 M perchloric acid was used as a blank. Standard concentrations of formaldehyde were prepared and the resulting curve was used to determine the concentration in the extracts in ug/ml. The resulting figure was multiplied by 4 to give mg/kg fish.

5.2.4 Assessment of Gel Properties

The moisture content of the gels was determined by drying in an air oven at 105°C for 18 hrs.

Gel Texture Evaluation Tests as described in Section 4 for the determination of puncture, torsion, folding and sensory properties of the gels were carried out on the gels.

5.2.5 Statistical Analyses

Analysis of variance and student's t-test were employed to evaluate data for the significance of the degree of variation and the difference between treatments using Minitab (Ryan et al,1982).

5.3 Results and Discussion

5.3.1 Effect of Frozen Storage on Fish Flesh

Table 5.1 shows the moisture and expressible moisture of H&G hoki flesh after frozen storage. No trend on storage is seen for the expressible moistures in agreement with the results gained by Kurokawa (1979) and Samson et al (1985). Bremner (1977) showed a loss of water holding capacity for cucumber fish but not

for the other species tested. He concluded that the test, using a higher centrifugal force of 50,000g for 60 min. than used in this study, was not sensitive to changes in the proteins on frozen storage.

Table 5.1 Moisture, expressible moisture, and K value of mince from H&G hoki stored for various times at -29°C

Storage Time (days)	Moisture (%)	Expressible Moisture (%)	K value (%)
0	-	-	19.3 (3.1)
35	82.6 (0.4)	13.0 (0.9)	12.1 (0.6)
104	81.1 (0.9)	12.2 (1.7)	9.6 (1.7)
188	81.9 (0.6)	11.2 (2.9)	17.3 (1.4)
202	81.9 (0.4)	12.9 (2.1)	-
260	82.5 (0.6)	12.8 (2.7)	11.3 (0.4)

Standard deviations are in brackets.

As expected, the K values showed no trend on storage and values were low showing the raw material fish were fresh, less than 4 days in ice. Hence the results of the day 4 samples from the chilled storage investigation (Section 4) are taken as day 0 (unfrozen) for this trial as the fish quality is of the same order as the fish used in this trial.

There was an initial increase in flesh .pH on freezing and then a decline on storage over the period of the trial (Figure 5.1). Similar decreases in pH have been reported for cod and haddock stored at -10°C and -18°C up to about 50 days storage, after which the pH increased again (van den Berg, 1964). This initial decrease has been attributed to the precipitation of alkaline salts, calcium, magnesium, and sodium phosphates. The lower storage temperature in this trial and consequent slower reaction rate would suggest that these results correspond to the initial portion of the curve of van den Berg.

There was a significant increase of formaldehyde in the hoki flesh after 100 days storage (Figure 5.1). The increases in formaldehyde for these H&G samples are as expected slower than those reported for hoki mince stored at -18°C (Bremner ,1980) where levels of about 100 mg/100g were found after 80 days.

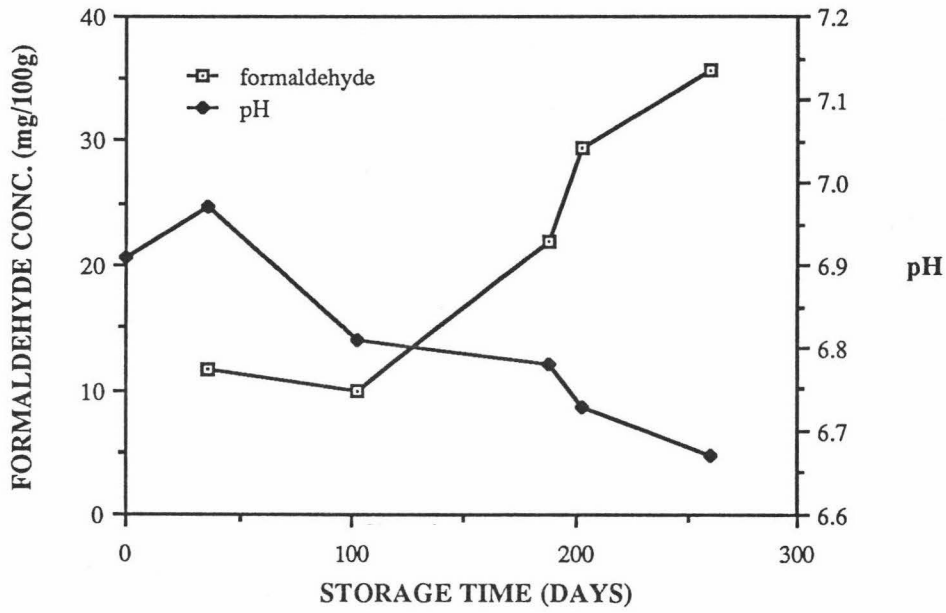

Figure 5.1 Changes in flesh pH and formaldehyde concentration in H&G hoki on frozen storage at -29°C

5.3.2 Changes in Gel Properties with Frozen Storage

For the gels made from unwashed mince the cooked gel moistures ranged from 77.9% to 78.8%. In the washed gels however, the moisture content in the 104 day samples were higher than the other samples which ranged from 79.1% to 79.8%. This was due to difficulty in dewatering the washed mince. There was no systematic variation in the moisture that could account for the observed changes in rheological properties over time.

Puncture Test. All treatments gave a significant decrease in both puncture deformation at failure and the gel strength on frozen storage of the hoki (Figures 5.2 and 5.3). High values were gained for the puncture deformation of washed samples at day 260, it is difficult to explain this variation, however it is worthwhile noting that the phenomenon has been reported by other researchers (Scott et al., 1988).

Apart from the chilled sample (time 0), there little difference in deformation between samples cooked at either 60°C or 90°C. This is in contrast to the results from the chilled storage trial where a difference was seen in the later stages of storage probably due to the leaching of enzymes from the gut region of the fish.This would suggest that hoki has little endogenous proteolytic enzymes active in the 50-70°C temperature range.

The strength of gels made from washed mince were generally greater than those made from the corresponding unwashed gels. This difference was more noticeable in the force component of the gel strength than the deformation component. The greatest decrease in both deformation and gel strength was seen in the first month of storage with the rate of decrease less after about three months storage.

These results show a similar trend to those of Scott et al (1988) for Alaska pollock stored at -29°C. However, in that trial the

Alaska pollock were stored for 2 weeks at -15°C prior to the trials start (day 0), thus the initial decrease over the first 100 days in deformation and gel strength apparent in the present investigation was not seen. The deformation and gel strength values gained in this trial for hoki were also higher for the corresponding storage time. Differences in gel preparation methods, and the slower probe speed used in the trial of Scott et al. (10 mm/min) compared to our study (20 mm/min) may account for some of these differences (see Section 3.2.1 for a discussion of the effect probe speed has on puncture results).

After 35 days storage the deformation of the W90 gel was 23% lower than that of the gels made from chilled hoki, and after 260 days 41% lower. The gel strength of the W90 gels decreased by 48% after 35 days storage and 75% after 260 days. Other investigators have noted a decrease in gel-forming ability resulting from frozen storage for other species. Tanaka et al. (1962) also found that the gel strength of Alaska pollock declined rapidly during frozen storage and was 33% to 55% lower after 3 months storage at -22°C. Lizard fish stored for 2 weeks at -27°C had only 50-60% of its gel-forming ability remaining when compared to fresh fish, but there was little further drop when stored for up to 2.5 months (Kurokawa,1979). Thus, the myofibrillar proteins in hoki appear to denature on frozen storage at a rate similar to that of Alaska pollock but slower than for lizard fish.

For the gels made from washed mince cooked at 90°C the gel strength was lower than the minimum for ship processed surimi of 680 g.cm (Okada and Tamoto, 1986) after 100 days storage (see Appendix 4 for a copy of the Japanese grading system).

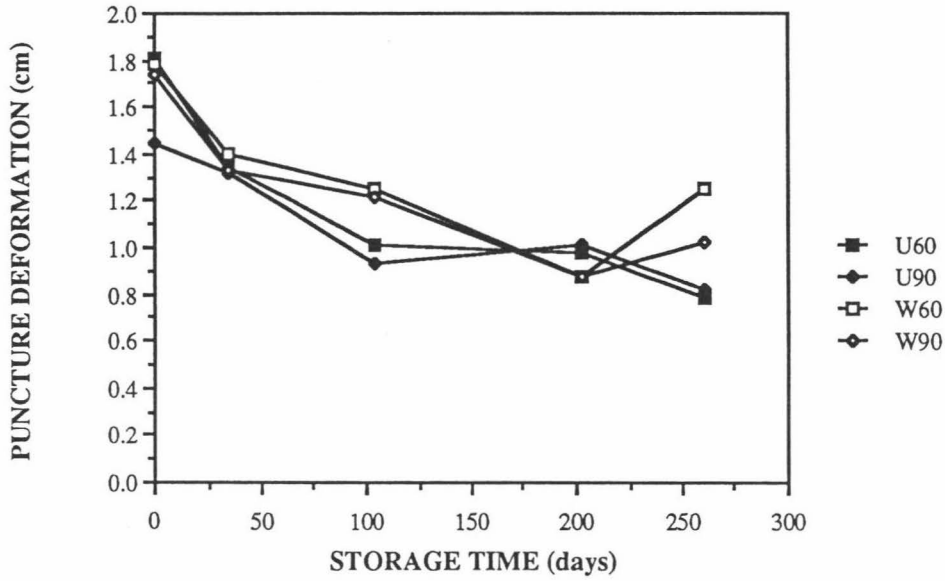

Figure 5.2 Changes in puncture deformation of gels made from H&G hoki stored at -29°C.

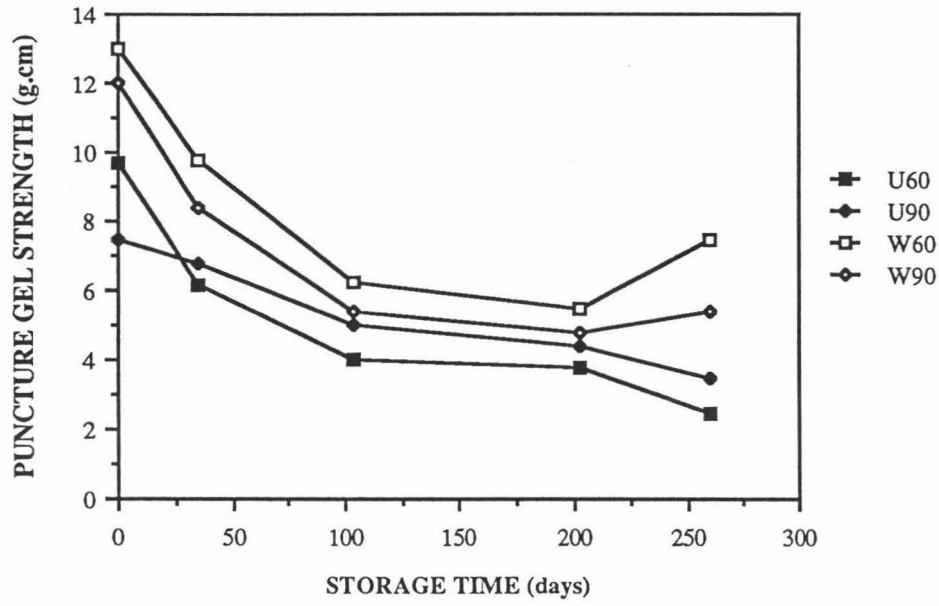

Figure 5.3 Changes in puncture gel strength of gels made from H&G hoki stored frozen at -29°C

Torsion Test The trends seen in the torsion results are similar to those for the puncture results. The shear stress and true strain values for gels made from washed minces were generally higher than those made from unwashed minces.

There was a significant decrease in true strain at failure values for all samples over the trial, see Figure 5.4. Other work has shown that the strain at failure is a good indicator of the functional quality of the proteins involved in gelation (Lanier, 1986; Kim et al., 1986; Lanier et al., 1985) and the results of this trial would support these findings.

True strain values did not differ significantly with the two heat treatments suggesting that protease effects were not significant.

The shear stress at failure values for the U60 gels showed a significant decline after 35 days and again after 260 days storage while the U90 and W60 gels showed an initial decline and then an increase on further storage (Figure 5.5).

A plot of rigidity against strain at failure has been suggested as a useful means of representing the rheological aspects important to surimi gels, such a plot shows that the gels tended to become less cohesive and more mushy or brittle on storage. Also, the unwashed gels generally had a lower rigidity compared to the washed mince gels and there was a consistent decrease in true strain over the trial (Figure 5.6).

Observations of the gels at failure during torsion testing showed that as the storage trial progressed and the samples became less cohesive the samples tended to fail due to shear (with the failure plane at right angles to the sample axis) rather than tension (failure plane 45° to the axis).

The decrease in strain and increase in stress with storage time suggests that there is a cross-linking occurring in the muscle with storage time which is being carried through into the gel.

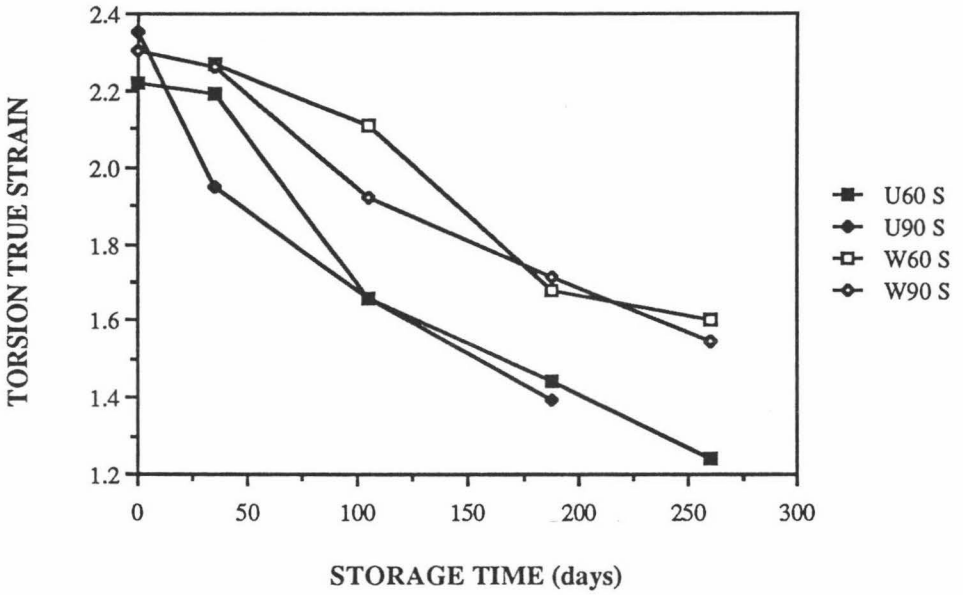

Figure 5.4 Changes in torsion true strain of gels made from H&G hoki stored frozen at -29°C

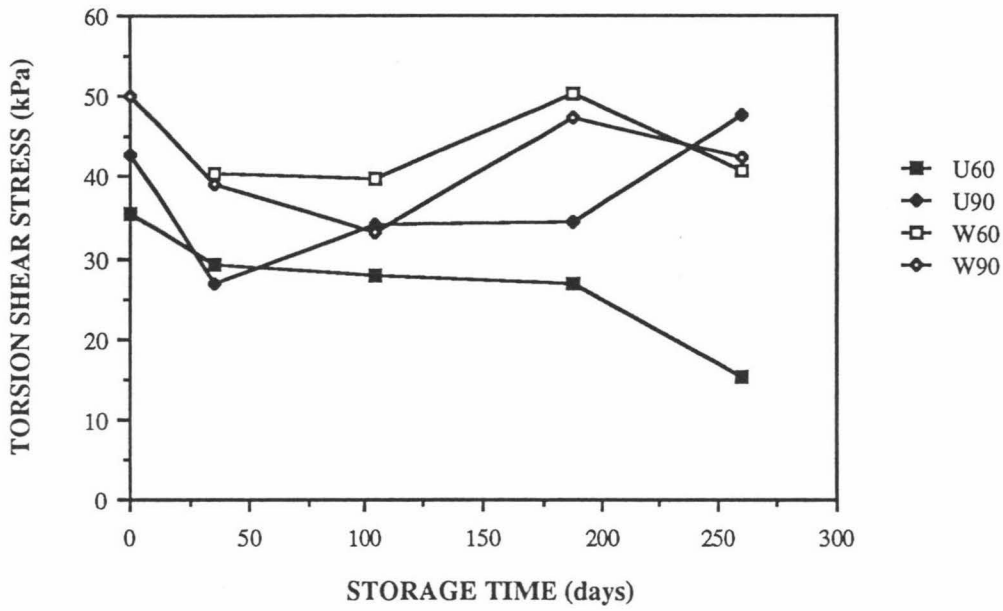

Figure 5.5 Changes in torsion shear stress of gels made from hoki stored frozen at -29°C

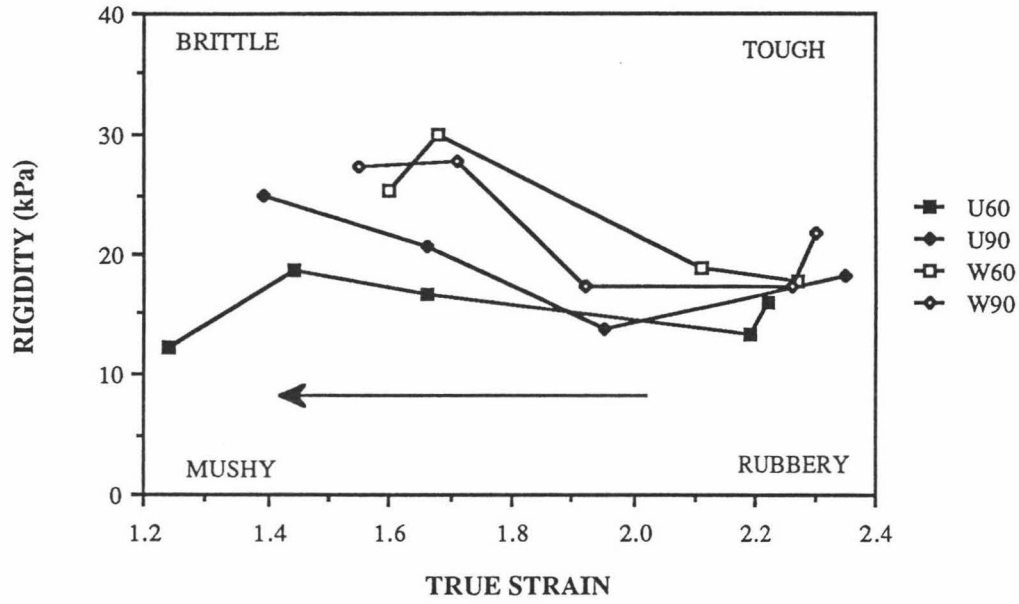

Figure 5.6 Torsion rigidity/strain plot. Arrow indicates the direction of changes in gel characteristics with storage time.

Sensory Texture Score and Folding Test. There was a decrease in sensory texture score over the time of the trial (Figure 5.7). This was similar to the trends seen in the results from the instrumental methods with the greatest decreases seen in the first 100 days of storage. The gels made from unwashed minces were scored lower at all sampling times. It is interesting that the gels cooked at 60°C were generally scored higher in the washed gels but were scored lower in the unwashed gels, this is in agreement with the puncture force and the torsion shear stress results and demonstrates the influence of the sarcoplasmic proteins on gel formation. The folding scores declined for the unwashed gels from 5 on day 35 to 4 for the U90 gel and 2 for U60 on day 100, higher than expected results for day 202 were gained with 5 for both gels and then both gels gave 2 on day 260. For the washed gels all scored 5 until day 260 when the W90 gel was scored 4. The fold test was less sensitive to changes resulting from frozen storage than the other texture tests.

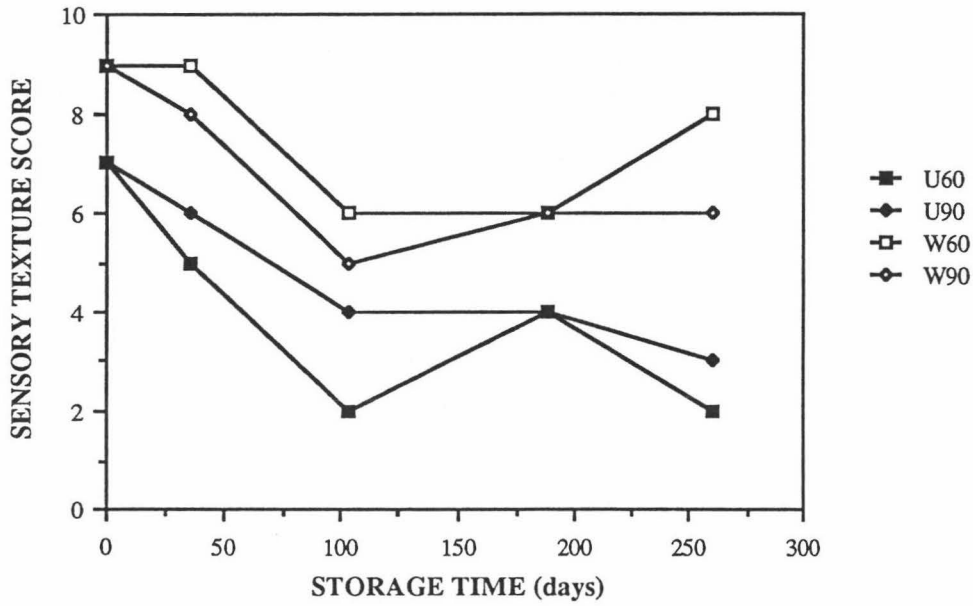

Figure 5.7 Changes in sensory texture score of gels made from H&G hoki stored frozen at -29°C

5.3.3 Correlations

Table 5.2 shows the correlation coefficients between the rheological tests on the W90 gels,the chemical tests on the flesh and storage time of the frozen H&G fish. Results from the W90 gels were used for this correlation because these gels were closest to normal surimi quality test procedures used in industry.

Flesh pH and formaldehyde concentration are highly correlated with storage time. True strain at failure was also highly correlated with storage time, pH and formaldehyde concentration. The deformation correlated with storage time and formaldehyde concentration, while force and gel strength correlated with time. Shear stress showed no correlation with other tests or storage time. Fold test scores were non-parametric so were not included in the correlation.

The pH and formaldehyde concentration of the flesh could be useful measurements to predict the gel-forming ability of the hoki as measured by torsion true strain.

Table 5.2 Correlation matrix of results of chemical and physical tests on mince from H&G hoki stored at -29°C for up to 260 days

	Storage Time	pH	Formald.	Deformation	Force	Strain
pH	-0.952					
Formaldehyde	0.948	-0.825				
Deformation	-0.878	0.758	-0.822			
Force	-0.809	0.738	-0.713	0.931		
Strain	-0.989	0.977	-0.899	0.863	0.840	
Stress	-0.024	-0.055	-0.062	0.205	0.484	0.078

$P < 0.01$, $r = 0.934$
$P < 0.05$, $r = 0.805$

5.4 Implications For An On-shore Operation

The storage of headed and gutted hoki at -29°C resulted in a significant loss of gel-forming properties over time. The gel strength of the washed gels cooked at 90°C decreased by 48% after 35 days and were less than the minimum for Japanese ship-processed surimi by about 100 days storage. It is probable that this loss of functional gel forming ability would be too fast to allow the use of frozen hoki for making surimi over an extended period in a commercial operation. Hoki appears to lose gel-forming ability with frozen storage at a similar rate to that of Alaska pollock.

Decreasing the storage temperature of frozen fish has been shown to reduce the rate of protein denaturation, as measured by total protein soluble in 5% NaCl (Love, 1962), it is possible therefore that storage at lower temperatures than used in this trial would slow down the loss of gel-forming properties of hoki. The advantages of increased storage life would have to be balanced against the increased capital and running costs of storage at these lower temperatures.

Measurement of the pH and formaldehyde concentration of the flesh were good indicators of the gel-forming ability of frozen stored hoki. The true strain at failure showed the highest correlation with storage time.

5.5 References

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6. EVALUATION OF RHEOLOGICAL METHODS

6.1. Introduction

Rheological tests form the basis of methods to assess the quality of surimi. The tests replace or supplement sensory testing during routine quality control procedures. Therefore, the test used should correlate well with sensory methods..

The strength of cooked surimi gels depends on the concentration and quality of functional protein. For samples with the same protein content and other ingredients, heat processed in the same way, changes in textural attributes should be primarily due to changes in myofibrillar protein quality. In this context, protein quality can be defined as the ability of the protein to form strong cohesive gels. The test should therefore correlate well with treatments that have been shown to cause denaturation of fish myofibrillar protein, such as time in chilled or frozen storage.

Ideally a method to be used for quality control purposes should be reasonably quick, simple and low cost to operate. The method should be able to be used routinely during steps in the process and be able to be performed within the necessary time limits for process-control.

In addition, there is a need for methods that are suitable for research, which ideally would not only correlate well with sensory methods, but would also have predictive capabilities and would thus facilitate the development of suitable rheological theory. Using this theory, analytical techniques such as linear programming, could then be applied to product formulation to manufacture products of a specified texture at least cost.

There has been much discussion in the literature as to the relative merits of the puncture and torsion methods for the testing of surimi (Lanier et al., 1985). The puncture method has been widely

adopted by the Japanese surimi industry and the torsion method has been proposed as the benchmark rheological test in the USA.

The studies described in Sections 4 and 5 on the effects of chilled and frozen storage on the gel-forming ability of hoki provide data from a wide range of fish qualities that would encompass most commercial situations. Consequently, the gels made from these fish cover a wide variety of textures; from strong, elastic to weak, mushy gels. Therefore, the results from these trials allow comparison of the puncture and torsion tests with each other, and with sensory and other chemical and physical tests over a range of gel textures.

The aim of this section is to compare the puncture and the torsion methods with respect to their correlation with a sensory test, accuracy, cost and convenience. Recommendations are made on the suitability of each test for use in industry.

6.2 Correlation With Sensory Tests

Most of instrumental parameters were highly correlated with the sensory scores ($p < 0.0005$), Table 6.1. Torsion rigidity however, was not significantly correlated. Generally the puncture test had a higher correlation with the sensory results compared to the torsion parameters with the puncture force value gave the highest overall correlation, Table 6.1.

One reason for the very good correlation with force was the design of the sensory score sheet used in this trial. The score sheet is used in the Japanese surimi industry and is ostensibly a single 10 point scale. The descriptors used refer to both gel hardness and cohesiveness attributes. Both attributes change over the scale in a concurrent manner, for example a score of 9 is described as strong and flexible, and a score of 3 is described as weak and brittle. This made the scale difficult to use when the gel parameters of hardness and cohesiveness changed independently,

for example, it would be impossible to place a soft but cohesive gel on this scale. Consequently, the panel may have emphasized the hardness attributes on the scale, and this may account for the very high correlation with puncture force. It is worthwhile noting that some Japanese researchers use the force parameter rather than a combined, force x deformation, gel strength value when reporting the results of studies on cooked surimi gels.

It is probable that gel cohesiveness was not measured to any great extent by the sensory test used in this study. The high puncture deformation correlation with sensory test score can be explained by its dependence on the force parameter ($P< 0.005$), Table 6.2.

The rigidity has been shown to be mainly influenced by moisture content in the gels, and therefore indirectly the protein concentration (Hamann and Lanier, 1986). Therefore, the low correlation of torsion rigidity with the sensory score is not unexpected as the moisture content of the samples over the trials was reasonably constant (80%). The higher correlation of the stiffness parameter is due to the dependence on the force. (Table 6.2).

Table 6.1 Correlation coefficients relating instrumental parameters to sensory texture score.

Punch Test	r
Force	0.915
Deformation	0.685
Gel Strength	0.838
Stiffness	0.899
Torsion Test	
Stress	0.629
Strain	0.697
Rigidity	0.180

Level of significance with 30 degrees of freedom

$P < 0.0005$, $r = 0.554$

$P < 0.005$, $r = 0.449$

$P < 0.01$, $r = 0.409$

Table 6.2 Correlation coefficients relating instrumental parameters

			Puncture		Torsion	
	Force	Deform.	Gel Strength	Stiffness	Stress	Strain
Deformation	0.839					
Gel Strength	0.976	0.908				
Stiffness	0.866	0.484	0.746			
Stress	0.577	0.261	0.479	0.739		
Strain	0.739	0.792	0.744	0.521	0.341	
Rigidity	0.055	-0.270	-0.042	0.353	0.758	-0.333

Level of significance with 30 degrees of freedom

$P < 0.0005$, $r = 0.554$

$P < 0.005$, $r = 0.449$

$P < 0.01$, $r = 0.409$

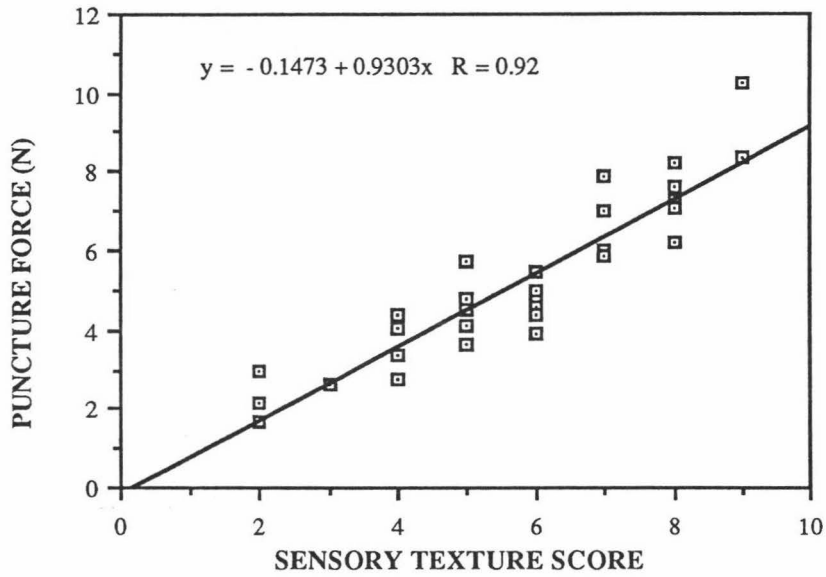

Figure 6.1 Relationship of puncture force to sensory texture score. Pooled results from Sections 4 and 5.

6.3 Accuracy Of The Tests

The precision of each method can be assessed by comparison of the coefficient of variation (standard deviation as a percentage of the mean) of the measured parameters over a wide range of samples. An analysis was carried out relating the mean value of each measured parameter to its standard deviation, the only parameter that was significantly dependent on the value of the parameter was puncture force ($p < 0.01$), Figure 6.2. Variation increased as the force value increased and standard deviations of up to 25% were found. The other parameters generally had standard deviations of less than 15%, with most being less than 10%.

The puncture test is a point determination which would increase the probability of encounting variation in defects in the gel. The torsion test however, fails along a plane thus reducing the effects of small defects on rheological measurements of the gel.

More replicates would be needed for the puncture test than for the torsion test to gain the same precision when testing strong gels.

This analysis demonstrates the large error associated with the measurement of failure properties in these gels. This has been noted in studies on other gel systems and has been attributed to failure taking place at a defect in the sample with the number and extent of such defects varying considerably from sample to sample (Mitchell, 1983).

In addition, Lanier et al. (1985) found that vacuum chopping can improve the level of precision of both the puncture and torsion tests. However, the reduced air content not only makes the gels more dense but also stronger, emphasizing the need for standard methods if results are to be compared from one laboratory to another.

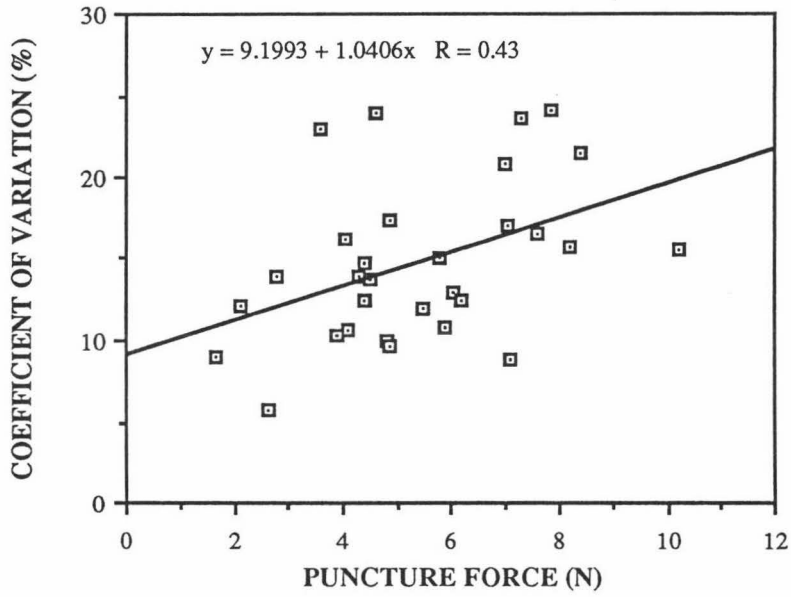

Figure 6.2 Relationship of puncture force to its coefficient of variation

6.4 Cost And Convenience

6.4.1 Time Requirement

Table 6.3 gives a breakdown of the estimated time to conduct each test. The analysis shows that while sample preparation time is essentially the same for both tests, the grinding and disc attachment steps of the torsion test result in a time requirement for the testing phase approx. 33% more compared to the puncture test.

The puncture test is quick, simple and very little training is required for an operator to competently carry out the test.

6.4.2 Cost Outlay

The equipment needed for preparation of samples is identical for both methods.

For the puncture test, the approximate cost of various machines that are readily available and suitable for use in quality control are:

Instron (model 1000)	$20,000
Stevens LFRA Texture Analyser	$13,000
Rheometer (Sun Scientific Instruments)	$14,000

At present no torsion apparatus is available commercially, however suitable apparatus can be constructed from a Brookfield, model 5XHBDT viscometer with attachments and a chart recorder:

Brookfield (model 5XHBDT)	$4,500
Attachments and grinding apparatus(to be made)	$1,500
Chart recorder	$1,500
TOTAL TORSION APPARATUS COST	$7,500

In addition, glue (Loctite, $12 for 20ml) and plastic disks (11.2 c per disk) are also required for torsion testing.

Overall, it may be concluded that the cost of equipment for torsion testing should be less than that for puncture testing, however the running costs would be slightly higher.

Table 6.3 Comparison of time requirements for testing of gel-forming ability

	Torsion	Puncture
Preparation		
- Prepare for cooking	1 hr	1 hr
- Cook, chill	1 hr	1 hr
- Clean up	1 hr	1 hr
Total preparation time	3 hr/lot	3 hr/lot
Testing		
- Calibrate/setup	5 min	5 min
- Cut, (glue)	35 min	10 min
- Grind	40 min	n/a
- Clean grinder	10 min	n/a
- Conduct test	30 min	30 min
Total test time	120 min	45 min
TOTAL TIME REQUIRED:	5 hr/lot	3 hrs 45 min/lot

Note: The times given in the above table are for testing one lot of surimi by one person. The samples are heated at two temperatures and 10 determinations are made per heat process.

6.5 Discussion

The puncture test is a quick and simple test suitable for use in routine quality control work. It is necessary however to have an appreciation of the limitations inherent in the method. The cost of equipment is reasonably high (approximately double that of the torsion test) however the running costs are comparatively low. The test generally correlates well with sensory properties of gels, although it is not precise when testing strong gels. Standard deviations of up to 25% of the mean force value were measured.

The use of a single "gel strength" measurement to describe gel properties is not recommended as at least two parameters are needed to describe adequately the textural properties of fish gels. A combined figure will tend to reduce the contribution of one of the measured values. It should be noted, that for the puncture test the force and deformation at failure are interdependent, thus the test is not able to fully describe the gel properties of cohesiveness and hardness. For the gels from the chilled storage study both cohesiveness and hardness decreased on storage so this limitation of the puncture test was not important. The gels from the frozen storage trial however, appeared to decrease mainly in cohesiveness with storage time and greater care would be needed to interpret data from the puncture test in this situation, particularly if only a single measurement is reported.

The torsion test is a more sophisticated test requiring more training (but not excessively so) and while not as fast as the puncture test it costs less to set up, and is more precise when testing strong gels. According to Lanier et al. (1985) torsion test precision can be improved further by the use of vacuum chopping and heating smaller diameter gels (to get more uniform heating through the sample cross-section) than used in these studies.

While the torsion parameters of stress and true strain at failure gave a significant correlation with the sensory texture score,

overall, the torsion test did not correlate as well as the puncture test.

The torsion test has the advantage of measuring shear stress and strain at failure, two independent measurements of the mechanical characteristics of the gel. These parameters are measured in fundamental units thus giving the test predictive capabilities that the empirical puncture test does not have. The test therefore has advantages over the puncture test when the results are to elucidate gel structure or when there is a need to specify surimi quality in precise legal terms. The results of the torsion test can be used in engineering applications such as equipment design, and in product formulation when it is desirable to use analytical techniques such as least cost linear programming. The use of a fundamental test will facilitate greater understanding of the relationship of the chemistry of gelation and gel structure to large deformation to failure criteria; ultimately the aim would be to develop surimi-based products with specific, carefully controlled consumer oriented textural attributes.

6.6 Recommendations

The puncture test is suitable for routine quality testing of surimi, however both the force and deformation results should be reported.

For research and when more accurate specification of quality is needed then the torsion test would be more appropriate.

Whichever method is used, it is imperative that the preparation and testing be carried out in a consistent and uniform manner to allow comparison and communication of results. There is a need for a standard industry-wide method for testing the gel-forming ability of surimi.

6.7 References

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Appendix 1 Torsion Method Calculations

A. Minitab Program

```
This programe calculates Tmax,Smax,True strain
and Rigidity
note Calibrated for the new F-Shirley
note cone speed = 0.5rpm
note chart speed = 4 mm/sec
let k1=301800
let c5 = (c1/2)/1000
note calc K
let c20 = sqrt(c5/.0075+1)
let c4 = (3*((1+c20)^2))/(4*(1+2*c20))
note calc R**3
let c6 = c5^3
note calc torque,Nm
let c7 = c2*.0000981
let c8=(c6/c4)*10000
note calc Stotal,rad
let c9 = c3*.0131
note calc Sspring,rad
let c10=c2*0.0045912
note calc Ssample,rad
subt c10 c9 c11
note calc Tmax,Pa
let c12=(2*(c4*c7))/(c6*3.1416)
note calc Smax
let c14=2*c4/((c13*c6)*3.1416)
let c21=c13/(c13+k1)
let c15=c14*(c11*c21)
note calc True strain
let c22=c15^2
let c23=sqrt(1+c22/4)
let c16=loge(1+(c22/2)+c15*c23)
note calc Rigidity
divi c12 c16 c17
name c1'Dia/mm' c2'Yaxis' c3'Taxis' c4'K' c5'R/m' c6'R**3' c7'M/Nm'
name c8'R3/K' c9'Stotal' c10'Sspring' c11'Ssample' c13'Q'
name c12'Tmax' c15'Smax' c16'TrueS' c17'Rigid'
outfile 'test.001'
note SAMPLE TORSION TEST RESULTS
NOTE TORSION RESULTS
print c1-c17
desc c12 c15 c16 c17
outf
end
```

B. Sample Output

SAMPLE TORSION TEST RESULTS

print c1-c17

Column	Dia/mm	Yaxis	Taxis	K	R/m	R**3
Count	8	8	8	8	8	8
Row						
1	20.200	692.000	390.000	1.183	0.010	1.03E-06
2	20.400	764.000	444.000	1.185	0.010	1.06E-06
3	19.000	452.000	312.000	1.174	0.009	8.57E-07
4	18.700	560.000	388.000	1.171	0.009	8.17E-07
5	17.700	532.000	364.000	1.164	0.009	6.93E-07
6	17.700	476.000	346.000	1.164	0.009	6.93E-07
7	15.200	262.000	256.000	1.143	0.008	4.39E-07
8	15.100	244.000	266.000	1.143	0.008	4.30E-07

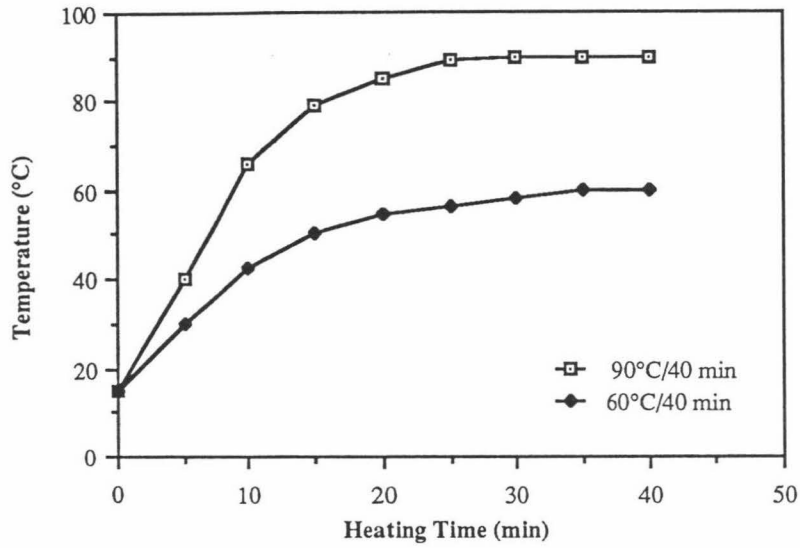
Column	M/Nm	R3/K	Stotal	Sspring	Ssample	Tmax
Count	8	8	8	8	8	8
Row						
1	0.068	8.71E-03	5.109	3.177	1.932	49626.1
2	0.075	8.96E-03	5.816	3.508	2.309	53262.6
3	0.044	7.30E-03	4.087	2.075	2.012	38647.3
4	0.055	6.98E-03	5.083	2.571	2.512	50123.1
5	0.052	5.96E-03	4.768	2.443	2.326	55774.9
6	0.047	5.96E-03	4.533	2.185	2.347	49903.8
7	0.026	3.84E-03	3.354	1.203	2.151	42621.2
8	0.024	3.77E-03	3.485	1.120	2.364	40457.8

Column	Q	C14	Smax	TrueS	Rigid
Count	8	8	8	8	8
Row					
1	5.7E+05	1.291	1.627	1.487	33383.1
2	5.5E+05	1.303	1.936	1.717	31015.1
3	7.1E+05	1.224	1.730	1.565	24690.0
4	7.6E+05	1.208	2.168	1.879	26677.4
5	9.3E+05	1.153	2.022	1.779	31359.5
6	9.3E+05	1.153	2.041	1.792	27855.0
7	1.6E+06	1.016	1.844	1.650	25827.5
8	1.7E+06	1.010	2.024	1.780	22734.0

desc c12 c15 c16 c17

Column	Tmax	Smax	TrueS	Rigid
Count	8	8	8	8
Average	47552.1	1.924	1.706	27942.7
Std.dev.	6217.5	0.179	0.130	3674.3
SE(mean)	2198.2	0.063	0.046	1299.1
Maximum	55774.9	2.168	1.879	33383.1
75% pt	52477.7	2.037	1.789	31273.4
Median	49765.0	1.979	1.748	27266.2
25% pt	40998.7	1.759	1.587	24974.4
Minimum	38647.3	1.627	1.487	22734.0
Range	17127.6	0.540	0.392	10649.1
TMean	47552.1	1.924	1.706	27942.7

Appendix 2 Heat Penetration Curves For Gel Cooking



The above curves are representative of the heating conditions at the center of gels submersed in a waterbath at 60°C or 90°C for 40 minutes in 48mm folded width casing. These heat penetration curves were derived by measuring the temperature at the center of a 30mm diameter polycarbonate syringe with ends removed and filled with surimi paste. After filling the ends were sealed with aluminium foil.

Appendix 3 Taste Panel Results For The Sensory Assessment Of Hoki Stored In Ice

Table1- Changes in Raw Attributes For Hoki in Ice

GENERAL APPEARANCE		Approx. Days in Ice
Score		
10	Eyes slightly sunken. Skin iridescent green, no slime. Gills rose red.	1
9	Eyes slightly opaque, greyness in pupil. No body slime.Gills maroon, cloudy slime.	2
8	Eyes flat. Body slime thin and watery. Gills, dark rose red, milky slime.	4
6	Eyes sunken, slightly bloodshot. Body slime thin, clear and watery. Gills mottled dark red with cloudy brown slime.	8
5	Eyes cloudy, bloodshot. Skin blue/grey, little thin brown slime, scales loose. Gills bleached at margins, slime thick and brown.	11
3	Eyes swollen and bloodshot or sunken and cloudy. Body pale insipid grey, bleached, slime thick creamy brown. Gills bleached in patches, thick brick red slime.	15
1	Eyes swollen and bloodshot, loose in sockets. Skin bleached, slime thick dirty yellow. Gills bleached in patches, thick red brown slime	21

Table 1 cont'd

ODOUR OF GILLS Score		Approx. Days in Ice
10	Seaweedy, distinct.	1
9	Oily, fresh celery, slight hessian	2
8	Tangy brine, fresh celery	4
6	Musty, wheatstack, mushrooms, strong	8
5	Musty, eels, mousy, fermenting grass.	11
4	Rotten grass clippings, rotten potatoes, turnips, not strong.	15
1	Rotting vegetables, sour, acidic.	21
FLESH AND GUT CAVITY		
10	Flesh white, translucent. Gut cavity pearly white, blood bright red.	1
9	Flesh similar, localized lime green bile staining on gut wall and roe. Belly lining shiny black.	2
8	Flesh pearly opaque turning pink. Gut softer, pinker. Belly lining becoming grey detaching.	4
6	Flesh pinkening, slight gaping. Gut staining obvious. Bile staining dull dark green.	8
5	Flesh generally pink. Gut sloppy.	11

3	Flesh very pink around belly, dull. Bile staining generalized, turning yellow. Belly lining turning brown.	15
0	Flesh reddened, turning yellow, some belly burst. Guts disintegrating, bile brown.	21

Table 1 cont'd

		Approx. Days in Ice
RAW TEXTURE		
Score		
5	Firm, elastic	1
	Softening, becoming flaccid.	2
4	Some gaping, lost resilience, flaccid.	4
3	Very soft, gaping	8
	Pasty, breaking up, little stickiness	11
2	Mushy	15
0	Paper mache, falling apart, wet watery.	21

Table 2 - **Changes in Cooked Attributes For Hoki Stored in Ice**

COOKED ODOUR		Approx. Days in Ice
Score		
10	Slight seaweed, slight tallow candle.	1
9	Thick, flounder, gurnard, boiled potatoes, not strong.	2
8	Wet wool, slight condensed milk, kumera.	4
6	Sweet, caramel, smoked fish, fishmeal, burnt.	8
5	Burnt milk, fishcakes, sour milk, onions, flat, sweaty.	11
3	Ammonia, urine, wet cardboard,	15
0	Slight burnt rubber, strong ammonia, acrid,	21
COOKED TEXTURE		
5	Slightly elastic, juicy, tender.	1
	Juicy, some chewiness, wooly, firm.	2
4	Stringy, firm, toughening.	4
3	Slightly dry, slightly sticky, short.	8
2	Dry, soft, very little stickiness, fibrous.	11
1	Wet, goes dry on chewing.	15
0	Dry, soft, like chewing newspapers.	21

Table 2 cont'd

COOKED FLAVOUR Score		Approx. Days in Ice
10	Sweet, meaty, characteristic of species.	1
9	Slight sweetness, flounder, characteristic of species, slightly sour	2
8	Neutral, loss of characteristic flavour, slight metallic, strong snapper flavour.	4
6	Neutral, cold mutton, metallic, sour, slightly "sweaty"	8
5	Faint turnip, cold chicken, raw peas,slight off flavours.	11
3	Sour, cold chicken aftertaste, raw peas.	15
0	Strong ammonia, difficult to taste.	21

Appendix 4 Japanese Quality Standards For Ship Processed Surimi

(From: Okada and Tamoto, 1986; Introduction to Surimi Manufacturing Technology, Overseas Fishery Cooperation Foundation)

Ship-processed Salt-free Surimi Quality Standards (Example)

Grade	Raw material test			Kamaboko test (starch added)				Kamaboko test (non-starch)			
Factory ship surimi salt-free	Moisture	pH	Impurities	Gel strength	Folding	Degree of Ashi	Whiteness	Gel strength	Folding	Degree of Ashi	Whiteness
	%		Score	g.cm 3% added	Score	Score	Degree	g.cm	Score	Score	Degree
1	75.0±0.5	7.0 <	10	900 <	5	10	60.0 <	680 <	5	10	46 <
2	75.0±0.5	7.0 <	9.0 <	900 <	5	9	59.0 <	680 <	5	9	45 <
3	75.0±0.5	7.0 <	8.0 <	850 <	4.5	8.0	58.0 <	640 <	4.5	8.0	43 <
4	75.0±1.0	7.0 <	6.0 <	700 <	4	6.0	55.0 <	520 <	4	6.0	38 <
5	75.0±1.0	7.0 <	5.0 <	600 <	3.5	5.0	52.0 <	440 <	3.5	5.0	35 <
6	76.0±1.0	7.0 <	4.0 <	450 <	3	4.0	50.0 <	310 <	3	4.0	32 <

Figures shown in Table are the minimum acceptable level of each property.