Journal of Food Engineering 29 (1996) 317–327
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0260-8774/96/$15.00 + 0.00

0260-8774(95)00077-1

Fracture Stress of Fish Meat and the Glass Transition

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(Received 23 May 1995; accepted 18 November 1995)

ABSTRACT

Freezing a high moisture food may involve the crystallization of pure water and therefore concentrate the solute, which sometimes forms a concentrated amorphous solution (CAS). The CAS may be formed via hot air drying as well, although most hot air dried foods available on the market are porous and/or in powder form and are inconvenient for use in fracture tests. In this paper, the traditional Japanese dried food 'katsuo-bushi', a highly smoked, dried fillet of bonito fish meat (which can be regarded as a CAS in itself) was used as samples to measure the compressive fracture stress. The compressive fracture stress of 0% moisture Katsuo-bushi was found to be constant at temperatures between 25°C and −196°C, and this value was comparable to that of 0% moisture CAS of completely frozen bonito meat estimated using a simple model for a frozen food. On the other hand, fracture stress of katsuo-bushi with 15–20% moisture changed greatly at temperatures between 0°C and −90°C, showing the feature of yielding. The temperature of brittle–ductile transition was different from the glass transition temperature as defined by DSC. Copyright © 1996 Elsevier Science Limited

INTRODUCTION

Knowledge of the mechanical properties of frozen food is needed for appropriate design and operation of food processes such as a cryo-mechanical separation (Hagura and Watanabe, 1991), comminution in the manufacture of reformed and restructured meat products (Dobraszczyk *et al.*, 1987) and cutting a large block of frozen tuna meat into pieces of reduced size (Okamoto *et al.*, 1994). Besides these direct uses, measuring mechanical properties also offers invaluable information to improve the understanding of the second order phase change in food materials from

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a glassy, brittle phase to ductile, rubbery phase (Parker and Smith, 1993; Nicholls *et al.*, 1995).

In a previous paper, we investigated the compressive fracture stress of tofu (a soy-protein-jelly food) which increased as the temperature decreased from −20°C to −100°C during which the crystallization of pure water might occur and therefore concentrate the soy-protein solution (Watanabe *et al.*, 1995a). Tofu was selected as the sample because its moisture content was easily varied. Using a simple model in which frozen tofu was regarded as a two-component (composite) system consisting of pure water ice and a concentrated amorphous solution (CAS), the compressive fracture stress of the CAS of tofu was estimated as 180 MPa, i.e. 7·2 times larger than that of pure water ice. In the present paper, we show that the CAS of food material yields such large stress values by measuring the fracture stress of a food which can be regarded as a CAS in itself.

The direct measurement of fracture stress of the CAS of tofu requires a specimen made of 'pure' CAS, which is separated from the pure water ice formed in the frozen tofu. Unfortunately, separation of water from frozen protein food always produces a porous or powdered product, which is unsuitable for the fracture test. However, CAS may be formed in food not only by freezing but also by hot air drying. Most hot air dried foods available in the market are porous and/or in powder form because these are advantageous for rehydration to use as food. However, the traditional Japanese dried food katsuo-bushi, a highly smoked, dried fillet of bonito fish meat is convenient for fracture stress measurement.

In the process of katsuo-bushi manufacturing, bonito is dressed, boiled and smoke dried. The smoke drying process requires about two hours drying per day and resting in the dark for the rest of the day to obtain an even moisture profile throughout the fillet. This regime is repeated for seven to ten days. The finished product, containing 15–20% moisture, has the appearance of a piece of dried wood with a polished, stonelike surface when it is broken. In cooking, very thin pieces of katsuo-bushi shaved off from the dried fillet by a tool such as a plane are used as a seasoning in soup or directly served with cooked rice.

As the appearance suggests katsuo-bushi may be in a glassy state at room temperature. This is supported by the observation of the glass transition as measured by DSC (Suzuki *et al.*, 1995). The glass transition temperature of katsuo-bushi ranged from 125°C to 170°C as the moisture decreased from 14 to 0%. In the present paper, fracture stress of katsuo-bushi was measured at temperatures between +25°C and −196°C by compression tests, which revealed the temperature and moisture dependence of failure stress and ductile–brittle transition.

MATERIALS AND METHODS

Materials

Sample materials used were bonito meat with a range of moisture contents (Table 1). Katsuo-bushi samples of finished product (Sample B) and those under the drying stage (Sample C) were obtained from Yanagiya Honten Co., Yaizu. Katsuo-bushi, cut to an appropriate size, was shaped into a cylinder (5 mm diameter, 10 mm long) using a lathe. Sample A was prepared by drying Sample B at 107°C until it reached a constant weight. In this paper, Sample A was regarded as having 0% moisture.

TABLE 1
Materials used for Fracture Stress Measurements

Sample		*Moisture content (% wt)*
A	Katsuo-bushi; additionally dried	0·0
B	Katsuo-bushi; finished stage	13·9
C	Katsuo-bushi; under drying stage	19·2
D	Cooked bonito; dehydrated	66·3
E	Cooked bonito	74·7

Samples D and E were of boiled bonito meat. Bonito purchased in the market was dressed, boiled for 30 min, cooled and crushed a little at a time in a porcelain mortar. The crushed meat was pressed into aluminum tubes (10 mm i.d., 20 mm long) and frozen at −30°C for 12 h. The crushed meat cylinders removed from the tubes were used as specimens for compression.

Apparatus and procedure

A universal testing machine (Model UTM4-200, Toyo Baldwin Co.) equipped with a custom made temperature controlling unit, which was described elsewhere (Watanabe *et al.*, 1995a), was used for uniaxial compression tests. A specimen, cooled with nitrogen gas, evaporated from liquid nitrogen contained in a Dewar vessel, was compressed between a pair of bearing plates at a constant rate of deformation (4·0 mm/min).

In the compression tests, the contact area between the specimen and the bearing plate considerably affects the result of the measurement (Tang *et al.*, 1994). When the specimen's surface is rough, it is forced to receive the load on a reduced contact area which causes fracture at an apparently lower load than that when the surface is smooth. Smooth contact is often achieved by 'ice capping', which involves introducing a small amount of cold water into the thin clearance on the test piece, the water soon freezes and the contact surface is smoothed (Hagura, 1991).

In this study, a pair of heads (aluminum disks: 8 mm diameter, 5 mm thick) were inserted between the specimen and the bearing plate in order to make it easy to apply ice capping to the upper end of the specimen (Fig. 1)(Wu *et al.*, 1976; Tang, 1995). When testing Samples D and E, ice capping was applied between the specimen and the head to smooth the contact. In the case of Samples A, B and C, however, a cyano acrylate adhesive was used instead of cold water to fill the clearance, because compression tests were conducted at non-freezing temperatures as well.

RESULTS AND DISCUSSION

Fracture stress of katsuo-bushi

Typical stress–strain curves for katsuo-bushi (Sample B) in compression tests under a constant rate of deformation are shown in Fig. 2. Katsuo-bushi (13·9% wt) showed

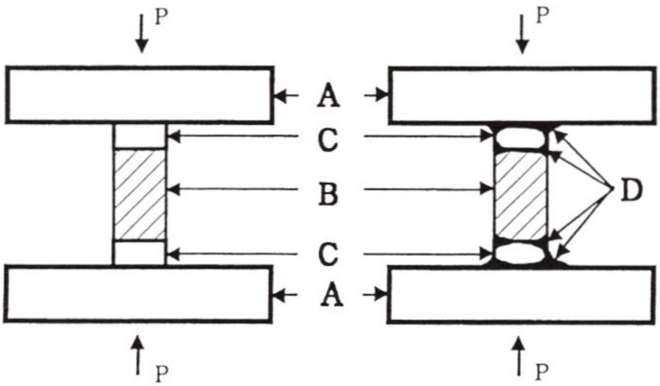

Fig. 1. Contact between specimen and bearing plate. A: Bearing plate, B: specimen, C: head, D: water (ice) or adhesive.

a ductile fracture in a range between 25°C and −75°C, while it showed an elastic deformation followed by a sudden fracture in a range between −90°C and −196°C.

The fracture stress, which in this paper refers to the maximum stress in a stress–strain curve, is plotted against temperature for katsuo-bushi Samples A, B and C (Fig. 3). The fracture stress of 0% moisture katsuo-bushi (Sample A) was constant over the whole range between 25°C and −196°C. This lack of temperature dependence is seemingly a characteristic of a pure substance as is measured for pure water ice (Watanabe *et al.*, 1995a). This is the first recorded time that a food material showed no temperature dependence on its fracture stress over the range between room temperature and −196°C. Using the Soxhlet extraction test using diethyl ether, Sample A was found to contain 2·1% wt lipid.

Complete drying (from Sample B to Sample A) caused a reduction in sample size: 7·1% reduction in diameter and 5·6% in height. The reduction in volume was, therefore, 18·6% which nearly corresponds to the volume of water (17·5%) removed. Hence, it seems no air bubbles were generated in the sample during freezing. This means that Sample A consists of 97·9% protein with some non-removable moisture and 2·1% lipid. In other words, Sample A can be regarded as a kind of CAS in itself.

Figure 3 shows the remarkable effect of moisture on the temperature dependence of compressive fracture stress of katsuo-bushi at subfreezing temperatures. Katsuo-bushi with 14% or 19% moisture showed a sharp increase in fracture stress when cooled from 0°C to −90°C. Since no ice melting peak was detected in the DSC rewarming curve of katsuo-bushi with 20% moisture from −100°C to room temperature (Suzuki, unpublished data), there may be no change in moisture content by freeze concentration during the whole range of temperature in the present fracture test.

The temperature dependence of fracture behavior in a material is usually explained by a combination of the ductile yield stress, which is greatly temperature dependent, and the brittle fracture stress which is slightly dependent on temperature as is shown in Fig. 4 (Ward, 1982). The brittle–ductile transition occurs at the intersection of the two curves on this figure. The temperature dependence of fracture stress of katsuo-bushi may be explained exactly in the same scheme. The increase in fracture stress during cooling from 0°C to −90°C corresponds to the increase in yield stress as is shown in Fig. 2. The constant fracture stress below −90°C may be regarded as the nature of brittle fracture. Thence, the measured fracture stresses shown in Fig. 3 suggests that the brittle–ductile transition occurs at about −90°C in katsuo-bushi with 14–20% moisture. The lack of yield stress in 0% moisture katsuo-bushi implys that the ductile–brittle transition is shifted to a higher temperature beyond 40°C. In other words, water molecules in katsuo-bushi may act as plasticizer to lower the temperature of brittle–ductile transition.

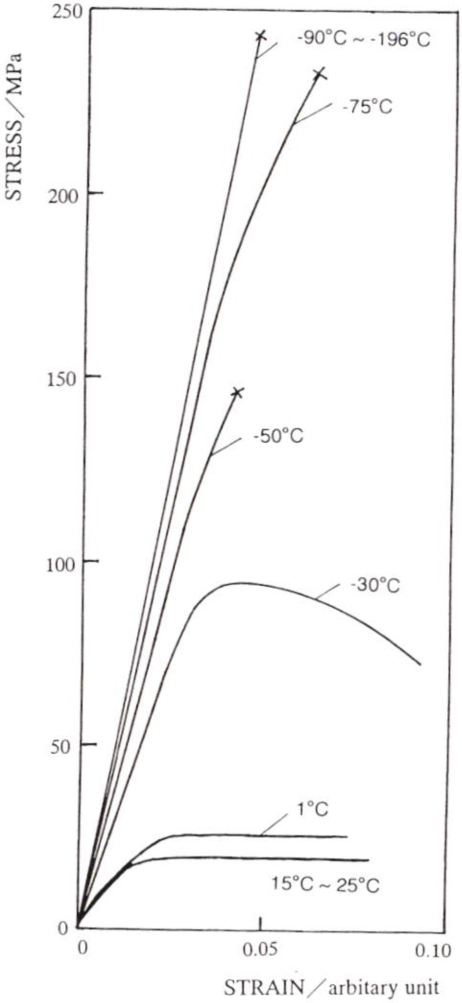

Fig. 2. Stress–strain curves under a constant rate of deformation for katsuo-bushi specimens (Sample B) at temperatures from 25°C to −196°C.

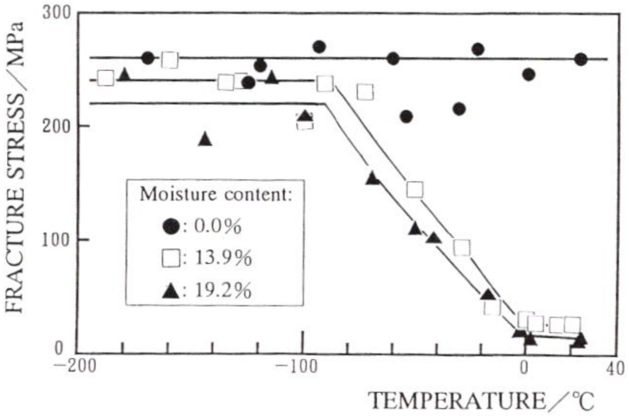

Fig. 3. Compressive fracture stress of katsuo-bushi measured using cyano acrylate adhesive to smooth the contact.

It should be noted that there is a remarkable difference between the transition temperature (−90°C) in katsuo-bushi as defined by brittle–ductile transition in this work and the glass transition temperature (125–170°C) as defined by DSC measured by Suzuki *et al.* (1995). The existence of the difference between the brittle–ductile temperature has been referred to recently by several researchers. Parker and Smith (1993) stated that whilst in certain cases the brittle–ductile transition coincided with the glass transition, this was generally not true. Nicholls *et al.* (1995) have clearly demonstrated that the brittle–ductile transition occurs within gelatinized starch whilst still in the glassy state as defined by the DSC. Kalichevsky *et al.* (1992) showed that various techniques (DSC, NMR, DMTA) measured transitions within

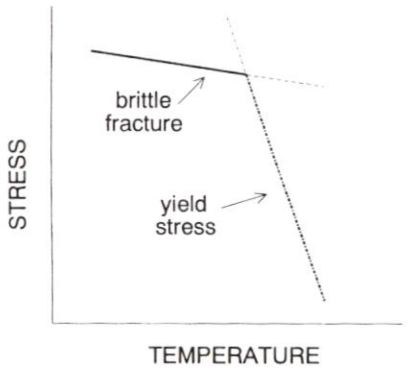

Fig. 4. Temperature dependence of brittle fracture and yielding. Brittle fracture and plastic flow are independent processes and whichever proceeds at the lower stress will occur. The brittle–ductile transition occurs at the intersection of the two curves.

amylopectin at different temperatures, which does not imply more than one transition but that the techniques are sensitive to different degrees of molecular mobility. We can guess that situation is similar in the fish protein system.

However, the question why the brittle–ductile transition temperature and glass transition temperature (DSC) differ from each other by as much as as 200°C remains unsettled. Answering this question may require lengthy and detailed experimentation because the brittle–ductile transition depends on a number of extrinsic factors including strain rate, temperature, stress state, specimen geometry and the presence of notches and flaws (Nicholls *et al.*, 1995; Atkins and Mai, 1986).

Fracture stress of CAS of cooked bonito meat

The compressive fracture stress of cooked bonito meat (Samples D and E) increased as the temperature decreased until it reached a plateau at about −90°C (Fig. 5). In the course of freezing a sample of cooked bonito meat with a high moisture content at 74% (Sample E), the crystallization of pure water may very likely occur and therefore concentrate the aqueous solution containing low and high molecular weight solutes. This solution, when it turns into solid, may be referred to as a 'concentrated amorphous solution' (Bellows and King, 1972). The temperature at which the maximal freeze-concentration takes place is the glass transition temperature, Tg'. The concentration of solute in this maximally freeze concentrated phase is referred to as the 'Cg' concentration' (Franks, 1985) when the solution is a simple aqueous solution. Since we are dealing with fish meat which maybe regarded as a pseudo-aqueous solution in this paper, we refer to this concentration as 'maximum freeze concentration', C^*.

The compressive fracture stress of CAS of frozen bonito meat may be calculated, assuming that the compressive fracture stress of a composite body is a volume fraction weighed average of those of components consisting the body. When the food is regarded as a two-component system consisting of pure water ice and CAS:

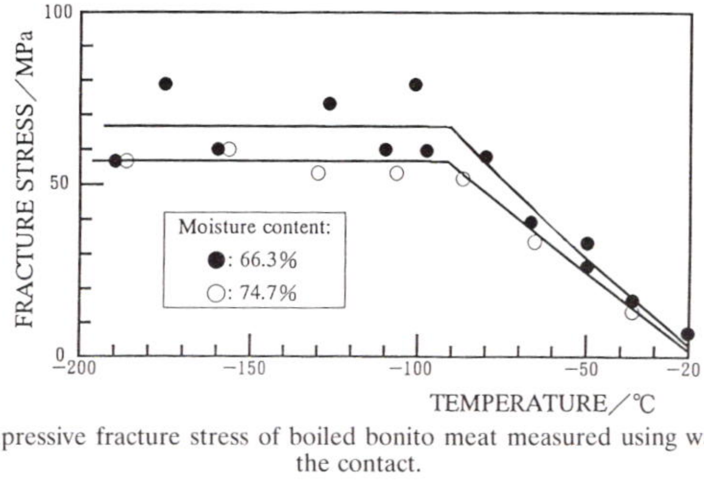

Fig. 5. Compressive fracture stress of boiled bonito meat measured using water to smooth the contact.

$$\sigma_{\text{food}}\frac{1}{\rho_{\text{food}}}=\sigma_{\text{ice}}\frac{\omega_{\text{ice}}}{\rho_{\text{ice}}}+\sigma_{\text{CAS}}\frac{\omega_{\text{CAS}}}{\rho_{\text{CAS}}}$$

where σ is compressive fracture stress, ρ is the density and ω is the weight fraction.

The fracture stress of bonito CAS relevant to the plateau at temperatures lower than −90°C, was calculated as 200 MPa when the maximum freeze concentration was set at 100%, i.e. 0% moisture. This calculated value is smaller than the measured fracture stress (270 MPa) of 0% moisture katsuo-bushi (Sample A). The possible reasons for this discrepancy are: (a) the size of specimens were different. The katsuo-bushi specimen was a cylinder of 5 mm diameter and 10 mm long, whilst the boiled bonito was of 10 mm diameter and 20 mm long. (b) The adhesive which was used to make the specimen and the head of the sample fit closely was different. Cyano acrylate adhesive was used for the katsuo-bushi (Samples A, B and C) while cold water was used for the boiled bonito meat.

The effect of size of the specimen on fracture stress was examined experimentally using polymethacrylic resin cylinders, which had different diameters but the ratio of diameter to height was kept at 0·5. The fracture stress was found to have decreased by 4·5% only (Fig. 6) as the diameter increased from 3 mm to 6 mm. Thence the difference in size of the specimen cannot be the cause.

The effect of contact between the specimen and the head has been discussed elsewhere (Tang *et al.*, 1994). In the present study the effect of contact was examined experimentally via compression tests of Sample A using ice capping instead of cyano acrylate adhesive at temperatures between −90°C and −180°C. The results of the experiment (Fig. 7) clearly show that the fracture stress of 0% moisture katsuo-bushi (Sample A), when ice capping is applied, reduced to 200 MPa which is equal to that of the calculated value for CAS of bonito meat with the assumption that the maximum freeze concentration is 100% solute. That is, the estimated fracture stress of CAS (0% moisture) of cooked bonito meat was directly validated and found to be reasonable by measuring the fracture stress of the CAS (0% moisture) of bonito meat. The value 200 MPa is very close to 180 MPa, the

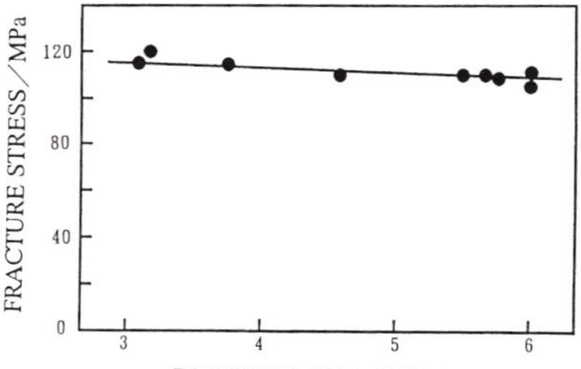

Fig. 6. Fracture stress of acrylic resin cylinders which have different diameters.

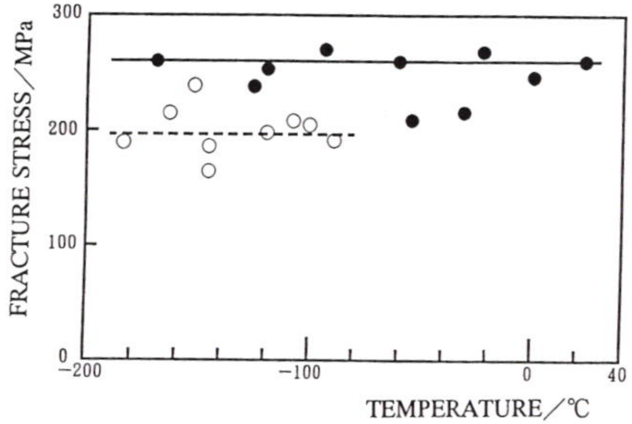

Fig. 7. Compressive fracture stress of Katsuo-bushi Sample A, measured using ice capping (○), or cyano acrylate adhesive (●) to smooth the contact.

calculated fracture stress of tofu CAS (0% moisture) at a temperature below −100°C.

In the actual freezing of boiled bonito meat, the obtainable maximum freeze concentration value is surely less than 100% solute because bonito meat dried to 81% solute (19% moisture katsuo-bushi), is reported to be in glassy state as measured by DSC (Suzuki *et al.*, 1995); this means no more concentration occurs. The maximum freeze concentration during freezing boiled bonito meat is not known yet. Supposing that this maximum freeze concentration is 70% solute (i.e. 30% moisture), the change in fracture stress of the CAS during a course of freezing boiled bonito meat can be speculated as is depicted in Fig. 8 in which the solid lines

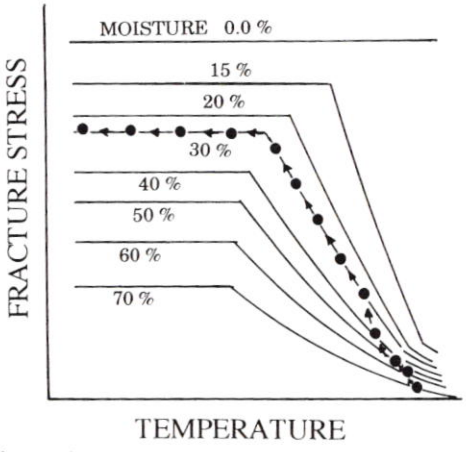

Fig. 8. A speculative illustration of the increase in fracture stress of boiled bonito meat during freezing.

refer to the fracture stress of boiled bonito meat with various moisture contents before freezing. Suppose that a boiled bonito meat with 70% moisture is cooled to a subfreezing temperature, some amount of pure water may crystallize, hence concentrating the solute, resulting in the emergence of a CAS. Lowering the temperature involves the concentration of the CAS, which increases the fracture stress of CAS, stepping up the equi-moisture lines as is shown by the arrows in Fig. 8. After the maximum freeze concentration C^* (30% moisture) is reached, the fracture stress of CAS may move up along the fracture stress line with the moisture corresponding to C^*.

When their compressive fracture stress (measured) at a completely frozen temperature (−120°C) is plotted against its initial moisture content (Fig. 9), smoked, dried bonito (katsuo-bushi), cooked bonito, dehydrated and non-dehydrated tofu (Watanabe *et al.*, 1995a), and distilled water are found to lie almost on a line from 25 MPa to 200 MPa. In this figure, the fracture stress of 13·9% moisture and 19·2% moisture of katsuo-bushi samples, which were measured using cyano acrylate adhesive to smooth contact, are plotted using their 74% reduced values, in order to make the comparison possible between the values measured using cyano acrylate adhesive and those using ice capping. The relationship shown in Fig. 9 suggests that the fracture stress of completely frozen food is governed by the fraction of ice and is little affected by the nature of the protein; such as the kind of protein or whether it is raw or heated.

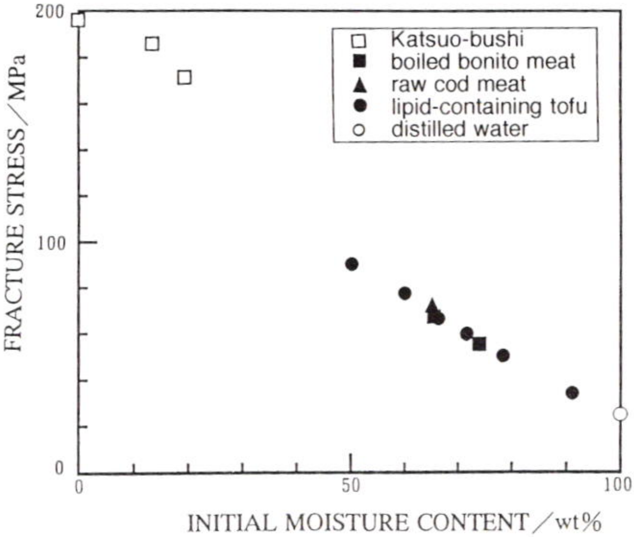

Fig. 9. Compressive fracture stress of completely frozen foods vs. initial moisture content. Ice capping using cold water was applied to measure the fracture stress of the samples: boiled bonito meat, raw cod meat, lipid-containing tofu, and 0% moisture katsuo-bushi. As for katsuo-bushi with 13·9% and 19·2% moisture, fracture stress was measured using cyano acrylate adhesive instead of cold water for ice capping. Thence its 74% reduced value is used in this plot for the comparison with that measured using cold water for ice capping.

ACKNOWLEDGEMENT

We wish to thank Hiroshi Masuda of Yanagiya Honten for his assistance in the preparation of Katsuo-bushi samples.

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