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Nuclear magnetic resonance (NMR) studies of water in fish meat jelly (kamaboko)

by Taneko Suzuki

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Nuclear Magnetic Resonance (NMR) Studies of Water in Fish Meat Jelly (Kamaboko)

Taneko SUZUKI

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Abstract: Using fish meat jelly (Kamaboko) made from iced croaker meat and Alaska pollack Surimi, physical state of water in Kamaboko was studied by 100 Mc proton high resolution magnetic resonance (NMR). The motional freedom of water molecule and the amount of water were estimated from the width and the area of NMR spectrum respectively, the following results were obtained.

Water in Kamaboko exists in at least two observably different degrees of order; one of which combines so tightly with the macromolecules in Kamaboko that it does not manifest spectrum of high resolution NMR (sweep width is about 1000 Hz), another shows the NMR signal and the line width of the signal is significantly broader than that of the signal produced by free water.

Comparing a starch-added Kamaboko with a no starch one, water molecues in the former were more restricted their freedom. In some Kamaboko samples, jelly strength and expressible water found correlated with the line width on NMR spectra, but others not. In conclusion the jelly strength or organoleptic quality of commercial Kamaboko may not be easily estimated from the line width of NMR spectra of water contained.

The changes of NMR spectra of the water during Kamaboko processing were observed: water were getting decrease their motional freedom during being ground with salt, and when the ground meat were allowed to stand to form gel, the water considerably bound showing much broader line width on NMR signal. However, after heating to make Kamaboko the line widths of NMR spectra became narrow again, this indicated increase of the freedom of the water molecule.

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Water contained in food plays an important role in determining the physical characteristics of food. This is to say, the ratio of free water and bound water in food probably is the major factor determining the physical constants of that food. For this reason, there have been various methods proposed to determine the state of water existing in foods or biological tissues.

One of these methods based on nuclear magnetic resonance spectroscopy (NMR) is recently gaining popularity because of its advantage that the protons of the water melecule can be measured within a short period and without damaging the samples[1-5]. The author previously found[6] that there were a number of water molecules with different degrees of resistance against dehydration in fish meat, by measuring proton NMR spectra of water in fish meat samples. p.48

In order to clarify the relationship between the physical properties of food and the state of water contained, the author has now examined by NMR spectroscopy the state of water contained in various fish meat jelly (kamaboko) samples, whose physical properties have been most extensively examined, because of its popularity among other processed fisheries products.

METHODS OF EXPERIMENT

Sample

A series of samples with different jelly strength were prepared by treating fish meat containg the same amount

with different
of water at different heating temperature and/heating times[7-8].

As raw fish meat, SA, A and C class salted Surimi* from Alaska pollack and iced croaker meat (a mixture of equal amounts of medium size white croaker and small white croaker) were used. For both Alaska pollack Surimi and croaker meat, the conditions of processing and the ratio of the ingredients are as follows. Namely, a mixture of 5 Kg of either Alaska pollack Surimi or water-bleached cooaker meat, 250 g of sugar, 250 g of sorbitol, 165 g of table salt, 100 g of mono-sodium glutamate, 450 ml of sweet sake was triturated for 30 minutes and the paste was placed in a molding tube and heated under the conditions shown in table 1.

(Table 1)

The meat of iced Alaska pollack was minced into small pieces, and bleached three times with five volumes of water, and the water was squeezed out with a piece of cloth. To the residue, table salt was added at 3%, and the mixture was grand well in a mortar. The paste obtained was wrapped with a piece of Saran Wrap, and stored in a refrigerator at 3 to 5°C overnight to set. The meat after this setting procedure was packed in an NMR sample tube, and heated at 85°C for 5 minutes inside the NMR probe, and then cooled to room temperature in the probe. This manufacturing procedure was taken as a standart model of

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*Translator's Note: minced fish meat after grinding.

production of fish meat jelly, and the NMR spectra of water in the fish meat prepared by various other processing methods were determined. Similarly, starch was added at 5% to the salted fish meat before molding in a tube, and heated at 85°C for 60 minutes to make the fish meat jelly. This product was taken as

control sample, the same salt meat being processed under the same conditions but without addition of starch.

Determination of Texture of Kamaboko

Jelly strength of the products was determined with an Okada jelly strength gauge, and expressible water with an expressible water meter[9].

Determination of NMR Spectrum

A 100 Mc high resolution NMR spectrometer (Nippon Denshi Co., Model Minimer 100) was used. The sample was chopped into small pieces and filled into a glass sample tube of 4 mm in diameter, and the spectrum was determined at room temperature. The degree of motional freedom of the proton of water molecule was shown by the half height width of the spectral peak of water, and expressed in Hz.

RESULTS AND DISCUSSION

State of Water in Kamaboko

In figure 1, NMR spectra of starched Kamaboko, non-starched Kamaboko, both prepared by the laboratory manu- p.

facturing methods, determined under identical machine settings are compared. In comparison to the width of the resonance line of pure water, the widths of the lines of the two Kamaboko samples, particluarly that of starched Kamaboko are extremely large. Taking the integrated value of the spectrum of the pure water as 100, those of the Kamaboko are 50 to 54. However, when the total water contents in both Kamaboko samples were determined, they were found in a range between 68 and 72%. Therefore, if all the water in Kamaboko was to have a high degree of motional freedom such as to be shown in this high resolution NMR spectrum, then the integrated peak area should have been between 68 and 72. As described above, the actual determination value was considerably lower than this expected value. Based on this observation, it is estimated that the water in Kamaboko must possess a structural configuration closely resembling that of a solid so that its peak is not shown in the high resolution NMR spectrum (sweep width 1080 Hz). Such water molecules are thought to be strongly bound to protein and starch molecules.

(Fig. 1 and 2)

Figure 2 is the NMR spectra of non-starched Kamaboko p. manufactured by the laboratory procedures. When about 0.2 ml of distilled water was added to the sample placed in a sample tube, and its spectrum was determined, the original spectrum A became peak B, which is a single peak considerably narrower than the original peak. However, if the distilled water was first sealed in a glass capillary and then the capillary holding the water

was inserted into the NMR sample tube containing the Kamaboko sample, spectrum C (shown in Fig. 2) in which the free water in the capillary and the bound water in the Kamaboko sample were shown separately, was obtained. These experiments clearly demonstrate that the protons of the bound water in the Kamaboko sample and that of the free water added to it are exchangeable. This same observation has been reported on water contained in muscles and gelatin[3,10]. When the Kamaboko was stored at -10°C for three months, and the water was expressed, the Kamaboko released a large amount of water and a sponge-like residue was obtained. When NMR spectrum of this sponge-like Kamaboko was measured, peak D of figure 2 was obtained. The peak appears to consist of a bundle of small sharp peaks, as if it were a spectrum of water sealed in a number of glass capillaries. Generally speaking, a mixture of water molecules with different degrees of motional freedom still exchange the protons of water molecules, and consequently, the peak width of the high resolution NMR spectrum of the mixture is shown as an average of the different degrees of freedom of the different water molecules. The wave-like results shown by peak D in figure 2 on the denatured Kamaboko by freeze-storage might have been caused by difficult proton exchange between the molecules of remaining water, but a more reasonable explanation must be expected from future studies.

These high resolution NMR spectroscopic results clearly demonstrate that the water contained in Kamaboko is not pure water but it is strongly bound. It is thought

that there are two different modes in this binding; one is due to the reaction between water and proteins and the other is due to some mechanical incorporation of water molecules into the mesh structure of Kamaboko. In addition to these, it is of course conceivable that there are water molecules which are so strongly bound that their protons are unavailable to magnetic susceptibility under the field strength of this high resonance NMR spectroscopy. Takagi[11] reported that, based on his results on the differential thermal analysis and the dry heat weighing assay, the water, both free and bound, in Kamaboko could be roughly classified into at least two different kinds depending on the degree of binding strength. It is, therefore, possible to obtain even more reliable informations regarding the state of water in Kamaboko, if the present NMR data are combined with the physical determination results such as those cited above.

Texture of Kamaboko and Degree of Freedom of Water

As shown in figure 3, there is a correlation between the peak widths in the NMR spectra of Kamaboko samples and the expressible water contents in the Kamaboko samples, when a number of different samples containg the same amount of total water are subjected to the testing. Namely, if the free water content is large in a sample, then the expressible water content in the sample is also large. It has been reported that the amount of expressible water is very well agreeable with the jelly strength and the score of sensory evaluation tentings of Kamaboko[9].

(Fig. 3)

(Fig. 4 and 5) p.51

Also as shown by figures 4 and 5, when a series of Kamaboko samples were subjected to NMR spectroscopic determinations, strong correlationships between the spectral peak width and the jelly strength and between the spectral peak width and the amount of expressible water were found. However, there are a few samples, of which the correlationship between the resonance peak width and the amount of expressible water is not clearly demonstrated, as shown by fig. 6 for SA class Surimi. This irregularity appears to show that the variation in the amounts of expressible water is not only dependent on the state of water contained in Kamaboko but also on the structure, that is, strength and roughness, of the meshes themselves that build the mesh structure of Kamaboko.

(Fig. 6) p.52

In commercially manufactured Kamaboko available at retail stores, the water contents vary widely, some contain starch, so that it may be rather difficult to estimate their jelly strengths and the scores of sensory test by determining their NMR spectral peak width.

Change of State of Water in the Kamaboko Manufacturing Processes.

In figure 7, the results of determination of peak width of NMR spectra of samples collected at each step of the experimnetal manufacturing Kamaboko are shown. As seen in the figure, the peak width broadens when the bleached meat is ground with salt, and this broadening is even more intense when it is subjected to setting. The setting appears to be some sort of process in which the physical structure of salted

and ground meat reduced gradually the freedom of water contained in the transitional structure. According to Niwa[12], the setting process corresponds to the stage of formation of hydrophobic bindings and of hydrogen bonds involving the water molecules. When the meat thus set is heated (result of which is the stat of so-called Kamaboko), the NMR spectral peak width becomes narrower than that of the set meat prior to heating, clearly indicating that the freedom of water increased again.

(Fig. 7)

This was probably caused by heat-denaturation of the p.5 proteins, which destroyed the protein structure that it had prior to heating, expelling the water contained in it before the heating. In fact, a visual inspection showed that the transparent gel became non-transparent when heated and that water came out of the gel. How these changes of freedom of water contained in fish meat, during the manufacturing processes, are related to what types of change of fish meat is one of the problems to be studied in the future.

CONCLUSION

The state of water contained in fish meat jelly (Kamaboko) was examined by means of proton high resolution nuclear magnetic resonance spectroscopy (NMR). The test samples were manufactured using iced croaker meat and Surimi of Alaska pollack. The degree of motional freedom of the water was evaluated from the peak width of the NMR

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spectral signal of water and the amount of water contained was estimated from the area of the peak in the spectrum. The following results were obtained.

1. There are two kinds of water contained in Kamaboko; one is strongly bound water, of which the protons are not shown as a signal in the high resolution NMR (sweep width 1080 Hz) and the other is, although shown as a peak in the NMR spectrum, restricted in motional freedom in comparison to pure water (Fig. 1).
2. In Kamaboko with added starch, the motional freedom of the water is much more strongly restricted than that of the water in Kamaboko without starch (Fig. 1).
3. Most of the Kamaboko samples show a reasonably good correlationship between the peak width of the signals in the NMR spectrum and the jelly strength and between the peak width and the amount of expressible water, However, it is tentatively concluded that it is difficult to estimate the jelly strength of Kamaboko by means of determining the peak width in NMR spectrum of any arbitrarily chosen Kamaboko (Fig. 6).
4. Determination of NMR spectra of intermediate samples at each step of the manufacturing process reveals the change in the state of water in fish meat during the manufacturing process, because the peak width broadens after grinding following the addition of salt, because it remarkably broadens after setting and finally narrows after heating (Fig. 7).

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Table 1. Processing method for several Kamaboko having different jelly strength and same amount of water.

Sample	Cooking temperature and period			
	First cooking		Second cooking	
	Temperature °C	Period min	Temperature °C	Period min
A	85	60	—	—
B	65	60	85	30
C	65	120	85	30
D	40	60	85	30
E*	85	40	—	—

* Cooking after setting (meat ground with salt was placed for 24 hr at 10°C).
Materials, iced croaker meat and A class Surimi from Alaska pollack.

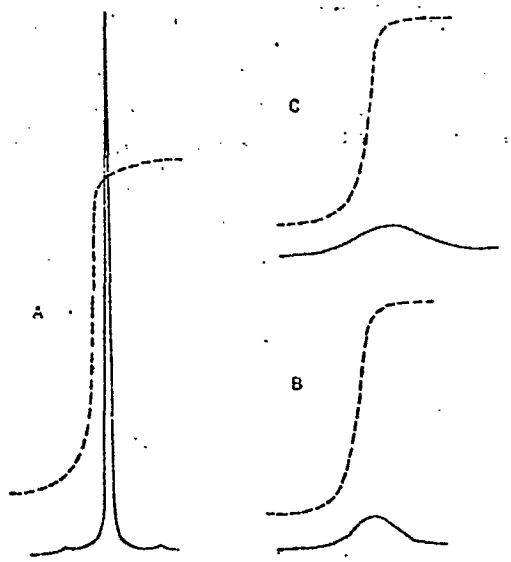

Fig. 1. High resolution NMR spectra and associated integrals of free water (A), Kamaboko without starch (B) and Kamaboko with starch (C). All spectra obtained using the same sample tube and machine settings. Sweep width=1080Hz

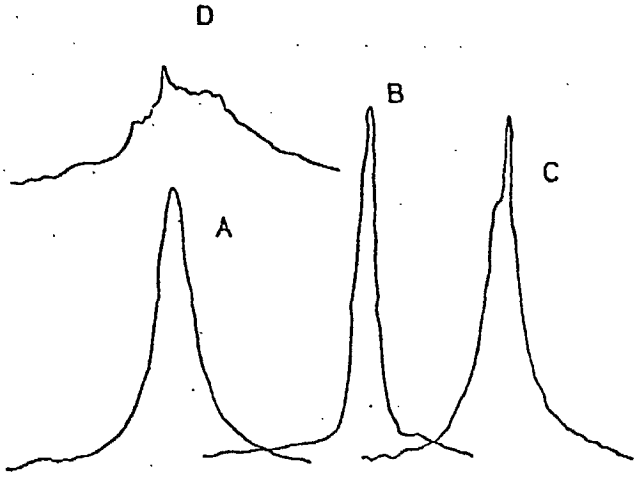

Fig. 2. High resolution NMR spectra of water in fish meat jelly (Kamaboko). A, Kamaboko alone B, Kamaboko containing pure water C, Kamaboko containing a capillary filled with pure water D, Kamaboko stored at —10°C for 3 months

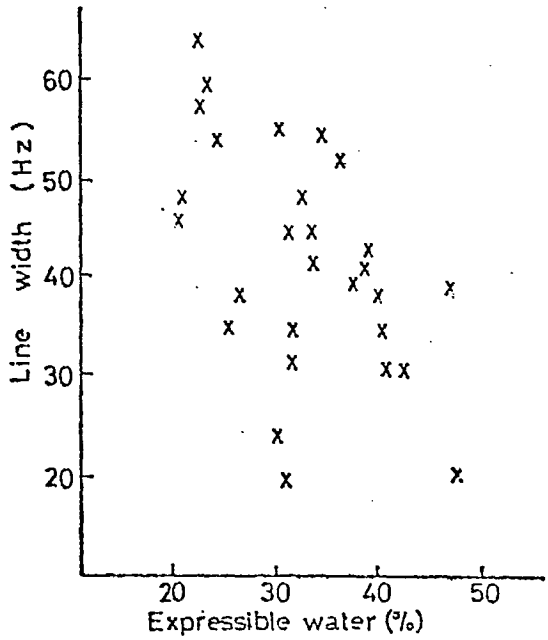

Fig. 3. Correlation between line widths of NMR spectra and amounts of expressible water from Kamaboko. $r=-0.6566$ $p<0.01$

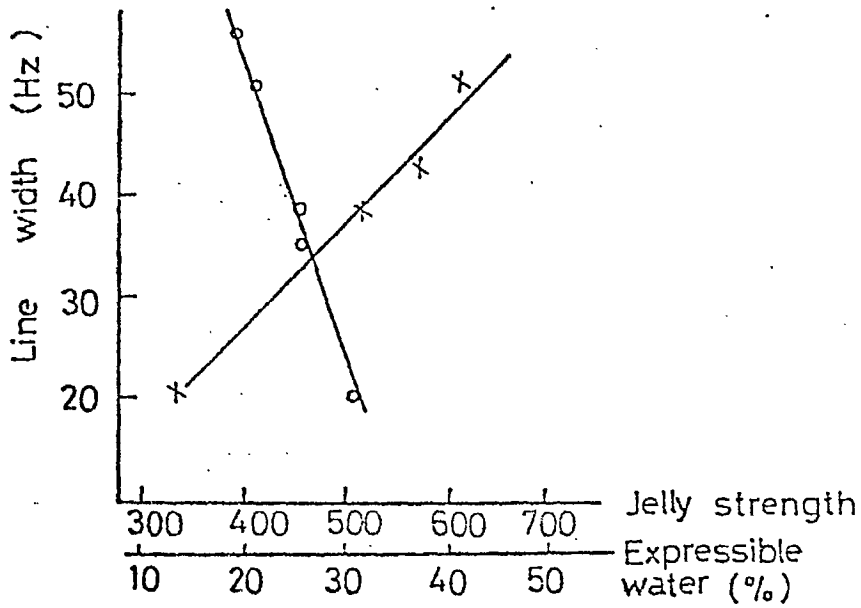

Fig. 4. Relation between line widths of NMR spectra and amount of expressible water (○) or jelly strength (×) of Kamaboko (Surimi A class from Alaska pollack).

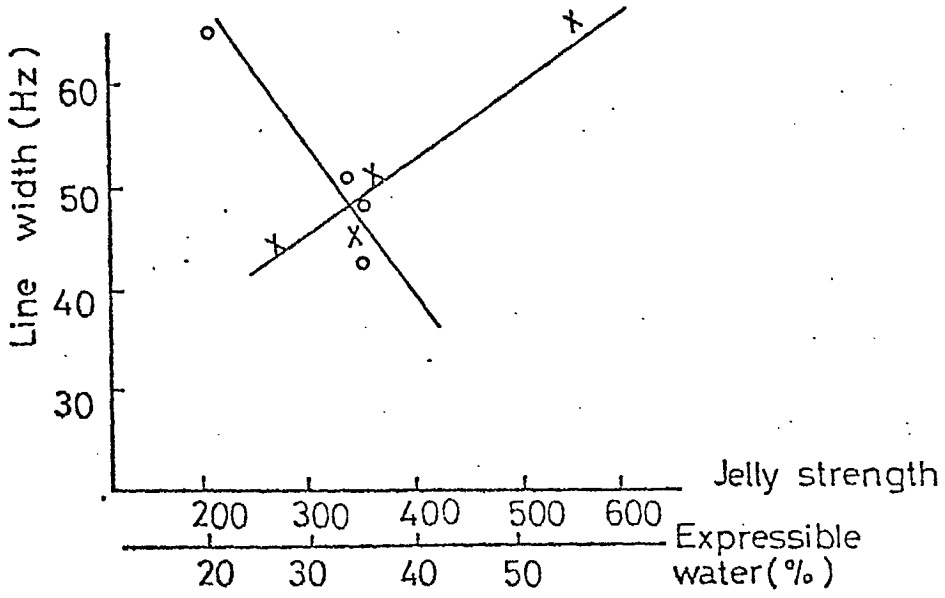

Fig. 5. Relation between line widths of NMR spectra and amount of expressible water (○) or jelly strength (×) of Kamaboko (croaker).

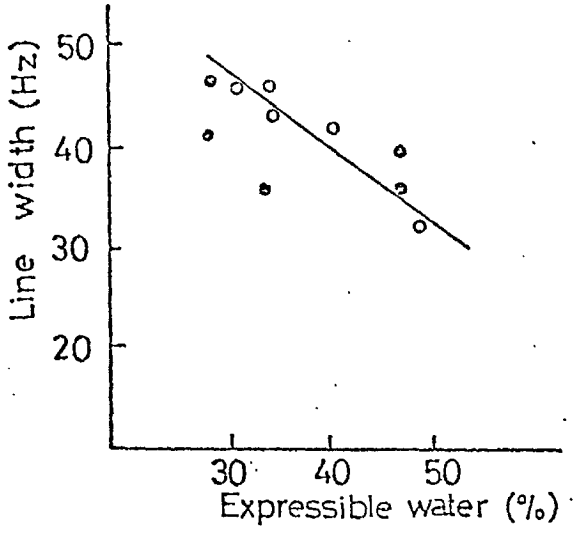

Fig. 6. Relation between line widths of NMR spectra and amount of expressible water of Kamaboko from Surimi (Alaska pollack). ○, Kamaboko from C class Surimi ⊙, Kamaboko from SA class Surimi.

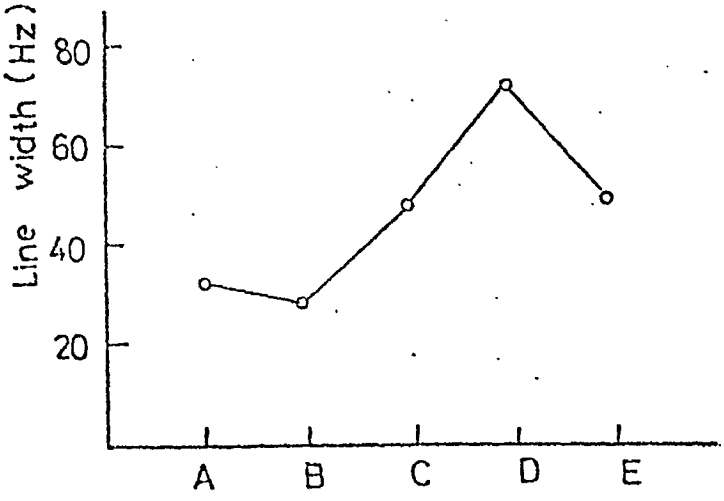

Fig. 7. Changes of line widths of NMR spectra during processing of Kamaboko. A, Fresh fish meat B, Rinsed meat C, Meat ground with salt D, Setting-meat (setting means jellification