

Effect of Added Water on Flow Property and Oil Droplet Size in Fish Meat Emulsion Containing Egg-Yolk

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Received February 16, 1996

Fish meat emulsion was prepared from egg-yolk, very low lipid sardine meat ground or suspended in weak alkaline solution, salad oil, and vinegar. The effect of added water on the flow properties and oil droplet size was investigated. In the ground-meat emulsion at an oil ratio of 1.1 to sardine meat irrespective of water ratio between 0 and 0.3, the hysteresis loop area of the flow curve was small and the small sized oil droplets were uniformly dispersed. When the oil ratio was increased to 1.6, the flow property changed within 1 day of storage. In the suspended-meat emulsion irrespective of the oil ratio of 1.1 or 1.6, the loop area was large with large oil droplets at water ratios of 0 and 0.1, and the area became smaller with smaller oil droplets at water ratios of 0.2 and 0.3. The emulsion with a water ratio of 0.1 was in the intermediate state between the irreversible shear breakdown and the thixotropy. At an oil ratio of 1.1 with this water ratio, both very large and moderately large loop areas were observed. At an oil ratio of 1.6, both the shear thinning flow and the shear thickening ones were observed during irreversible breakdown. The smaller oil droplets were dispersed more uniformly in the sample which showed a moderately large loop area or the shear thickening type breakdown.

Keywords: fish meat emulsion, added water, egg-yolk, flow property, oil droplet size

Nutritional substances are richly contained in sardine meat. In our previous study (Nakayama *et al.*, 1992), a new fish meat emulsion was produced from very low lipid sardine minced meat. This emulsion was odorless, cream-colored, and excellent in taste and consistency. When egg-yolk was used as an emulsifier, the fish meat emulsion was stable during shear applications and also during the storage (Nakayama *et al.*, 1993a). When egg-white was used as an emulsifier, a shear-unstable emulsion with a large yield stress was formed, and the yield stress was further increased during storage (Nakayama *et al.*, 1995). In the fish meat emulsion with the addition of egg-yolk, the shear stability was influenced by the relative amount of egg-yolk and oil. The fish meat emulsion with a yolk ratio of 0.1 to sardine meat¹⁾ was shear-unstable and the emulsion with a ratio between 0.3 and 0.6 was shear-stable (Nakayama *et al.*, 1993a). In the emulsion with the ratio of 0.2, shear-unstable and shear-stable samples coexisted. At a low oil ratio, the structure of the fish meat emulsion was stable during the shear application, but at a high oil ratio, it became unstable (Nakayama *et al.*, 1993b). Many large oil droplets were observed in the fish meat emulsion with a low yolk ratio and in the one with a high oil ratio.

Another factor which influences the shear stability of the fish meat emulsion is the amount of added water. In the present study, the fish meat emulsion was prepared from very

low lipid sardine minced meat, and the effects of added water on the flow properties and oil droplet size were investigated from the viewpoint of shear-stability improvement. When a vegetable salad was dressed with this emulsion or this emulsion was spread on bread, the shear-stability improvement by the addition of water was effective for preventing oil separation and irreversible shear breakdown.

Materials and Methods

Very low lipid sardine minced meat Two new types of very low lipid sardine minced meats (Nakayama *et al.*, 1995; Nonaka, 1990) were prepared at the pilot plant of Taiyo Fishery Co., Ltd. in Nagasaki prefecture, as shown in Fig. 1. Minced meat from fresh sardines was ground with 4 volumes of a 0.1% NaHCO₃ and 0.1% NaCl solution kept at 5°C or suspended in the same solution to remove lipids and blood. After the removal of bones and skin by filtration through a refiner, the ground meat was dewatered to 77.3% moisture by centrifugation. Without the filtration through a refiner, the suspended meat was dewatered to 73.5% moisture by centrifugation. The ground or suspended meat thus obtained was mixed with sorbitol, and subjected to frozen storage at -40°C. The two types of very low lipid sardine minced meat produced through the grinding or suspending processes were designated PMM-A and PMM-B, respectively, as an abbreviation for Purified Minced Meat. An analysis of these PMMs showed the following composition:

PMM-A: moisture 73.3%, protein (myofibrillar fraction) 19.6%, lipid 1.1%, ash 0.8%, carbohydrate (sorbitol) 5.0%.

PMM-B: moisture 69.7%, protein (myofibrillar fraction) 22.5%, lipid 1.8%, ash 0.8%, carbohydrate (sorbitol) 5.0%.

Manufacturing of new type emulsion A new type

¹⁾ In this report, the amount of emulsion constituents (e.g. egg-yolk, salad oil, vinegar, and added water) was described as the ratio to sardine meat. Hereafter, only the ratio is written in order to avoid the repeated expression to sardine meat. If necessary, the type difference of very low lipid sardine minced meat was specified for the presentation of a ratio.

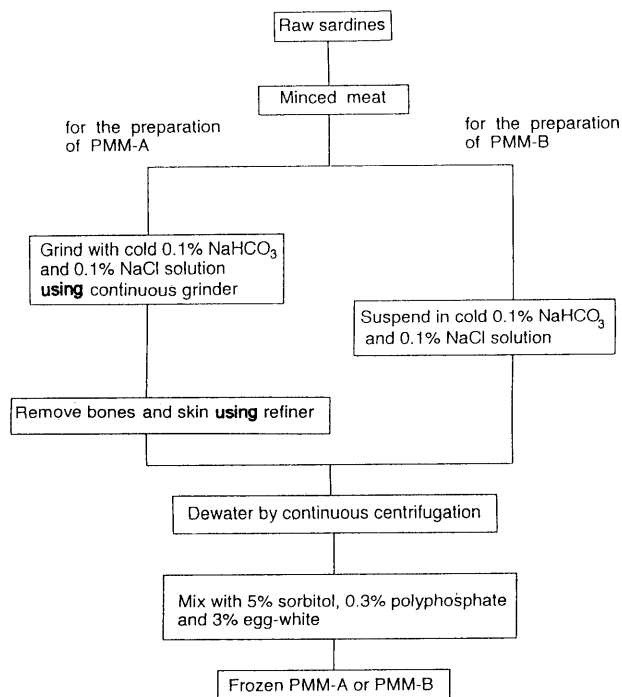


Fig. 1. Outline of procedure for processing Purified Minced Meat (PMM, very low lipid sardine minced meat).

emulsion was prepared from PMM-A or PMM-B as previously reported (Nakayama *et al.*, 1992, 1993a). As an emulsifier, egg-yolk was used. To change the moisture content of the emulsion, the ratio of the water added to PMM-A or PMM-B was set at 0, 0.1, 0.2, and 0.3 (Nakayama *et al.*, 1994). The constituent ratio of the fish meat emulsion was

PMM-A or PMM-B : egg-yolk : salad oil : vinegar
= 1 : 0.7 : 1.1 or 1.6 : 0.33

Storage of new type emulsion The sample emulsion was stored at 5°C in a cold room. The rheological parameters, which were obtained from the PMM-A emulsion with a water ratio between 0.1 and 0.3 at an oil ratio of 1.1 and the PMM-B emulsion with a water ratio of 0.2 and 0.3, irrespective of the 1.1 or 1.6 oil ratio, remained almost unchanged for 40 days of storage. These parameters of the PMM-A emulsion with no added water at an oil ratio of 1.1 and PMM-B emulsion with a water ratio of 0 and 0.1 irrespective of the 1.1 or 1.6 oil ratio slowly changed during the 40 days of storage. The remarkable change in parameters was detected within 1 day of storage in the PMM-A emulsion with a water ratio between 0 and 0.2 at an oil ratio of 1.6. In the present study, the sample emulsion stored for just 1 day was used to measure the flow property and observe the microstructure because the effect of added water to all the samples was discussed under the same storage conditions.

The pH of all the sample emulsions was 4.8, and remained unchanged for 40 days of storage even though some emulsions showed a change in the rheological parameters as described above.

Measurement of flow property The shear rate sweep measurement was carried out using a cone-and-plate rheometer (NRM-100, Nihon Rheology Kiki Co., Ltd., Funabashi)

with a cone (top platen) having an angle of 3° and a radius of 3.68 cm. The plate (bottom platen) of the instrument was thermostatted at $5 \pm 0.2^\circ\text{C}$. The maximum shear rate was 200 s^{-1} , and the sweep times taken for the increasing shear rate curve (hereinafter called up-curve) and the decreasing shear rate curve (down-curve) were both 100 s.

The power law equation is often used to express the flow property during the shear rate sweep measurement. The equation is written as:

$$p = B\dot{\epsilon}^n + C \quad (1)$$

where p is shear stress (Pa), $\dot{\epsilon}$ is shear rate (s^{-1}), B is the consistency index ($\text{Pa}\cdot\text{s}^n$), C is yield stress (Pa) and n is the flow behavior index. This equation was adopted to express the data in the low shear rate range or over all shear ranges. The three parameters, B , C , and n , were determined by the least-squares method, and compared between the fish meat emulsions with different amounts of added water.

Microscopic observation The prepared slides of a new type emulsion were observed under a microscope (OPTIPHOT, Nikon Co., Ltd., Tokyo) with a 40× objective and a 10×ocular. Photographs were taken with an automatic photographic system (MICROFLEX AFX-IIA, Nikon Co., Ltd.).

Results and Discussion

Difference in flow property of fish meat emulsion with the addition of water The time dependent flow of emulsions composed of egg-yolk, PMM-A, and vinegar with various amounts of added water is shown in Fig. 2. Almost all the experimental points of each flow measurement existed on the curve drawn by the power law Eq. (1) irrespective of the different amounts of added water at an oil ratio of 1.1. When the oil ratio was increased to 1.6, a distinct deviation of the experimental points from the power law curve was found only in the increasing shear rate for the emulsion with no added water. This deviation would be due to the lack of a homogeneous dispersion of increased oil droplets in the PMM matrix with low moisture content and the resulting irreversible shear breakdown. At an oil ratio of 1.1, the hysteresis loop area surrounded by the up-curve and down-curve was small in all the emulsions and was found between 0.38×10^4 and $0.56 \times 10^4 \text{ Pa}\cdot\text{s}^{-1}$ (also refer to the left of Fig. 5). At an oil ratio of 1.6, the area was extremely large around $1.55 \times 10^4 \text{ Pa}\cdot\text{s}^{-1}$ in the emulsion with no added water and very small below $0.35 \times 10^4 \text{ Pa}\cdot\text{s}^{-1}$ in the emulsion with an added water ratio between 0.1 and 0.3. The flow property without restoration after the rest period of 1 h was regarded as the irreversible shear breakdown. The flow property was the irreversible shear breakdown in the emulsion which showed a hysteresis loop area larger than $1.25 \times 10^4 \text{ Pa}\cdot\text{s}^{-1}$. Refer to the flow behavior index section concerning the repetition of shear rate sweep measurements after the rest period.

The emulsion at an oil ratio of 1.6 was unstable during storage. Even with an added water ratio of 0.1 and 0.2, the flow property changed within 1 day of storage, and the flow curve with a large loop area between 1.25×10^4 and $1.43 \times 10^4 \text{ Pa}\cdot\text{s}^{-1}$ was also obtained, as shown in Fig. 3. This result was ascribed to the smaller myofibrillar fragments (Nonaka, 1989;

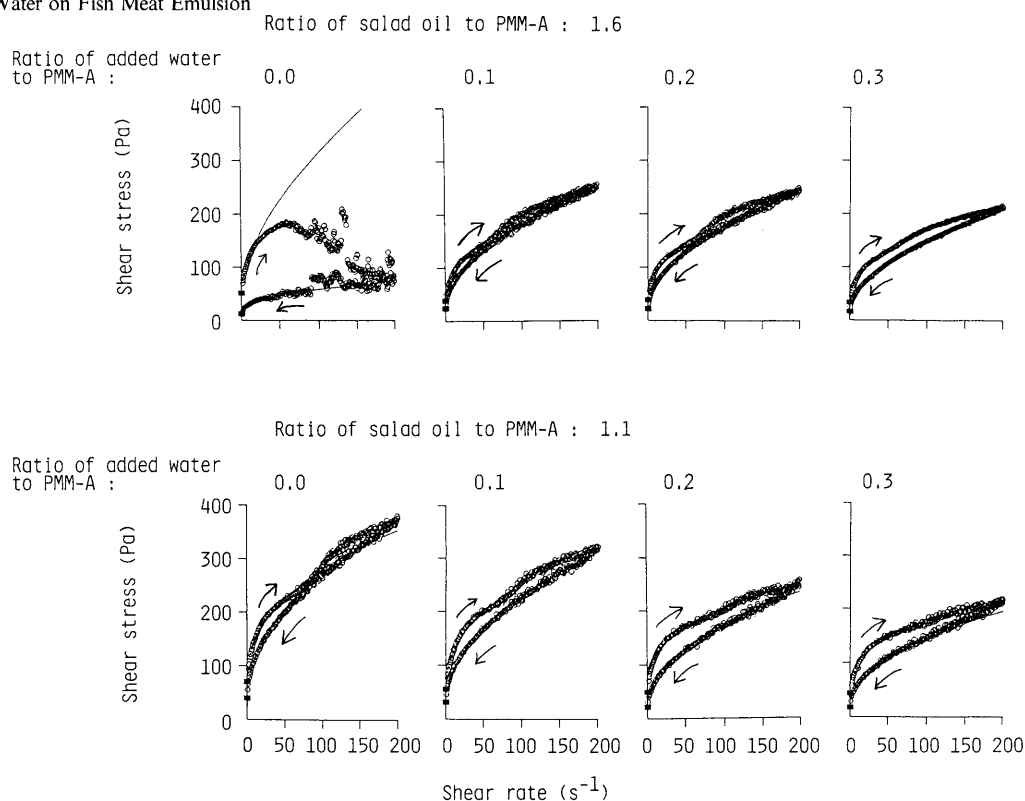


Fig. 2. Effect of added water on flow curve of fish meat emulsion with oil ratio of 1.1 and 1.6 prepared from PMM-A. The arrows along the experimental points indicate an increase or decrease in the shear rate during a continuous experiment.

Nakayama & Tomita, 1996) in the PMM-A matrix, which could not retain the small sized oil droplets for a long time. A further discussion from a microscopic viewpoint will be made later.

The time dependent flow of emulsions composed of egg-yolk, PMM-B, and vinegar with various amounts of added water is shown in Fig. 4. A distinct deviation of experimental points from the power law curve was found with the increasing shear rate when the added water ratio was 0 and 0.1 irrespective of the oil ratio of 1.1 or 1.6. This deviation resulted in the large loop area between 1.75×10^4 and 2.96×10^4 $Pa \cdot s^{-1}$ (also refer to the right of Fig. 5). When the added water ratio was increased to 0.2 and further to 0.3, almost all the experimental points of each flow measurement existed on the power law curve, and a small loop area between 0.42×10^4 and 0.64×10^4 $Pa \cdot s^{-1}$ was exhibited.

In the emulsion with an added water ratio of 0.1, some samples showed typical irreversible shear breakdown, while other samples showed an intermediate flow behavior between the breakdown and the thixotropy. At an oil ratio of 1.1, the emulsion showed two types of loop areas: a very large one ($2.86 \pm 0.30 \times 10^4$ $Pa \cdot s^{-1}$) and a moderately large one ($1.86 \pm 0.20 \times 10^4$ $Pa \cdot s^{-1}$). At an oil ratio of 1.6, the emulsion also showed two types of loop areas which were ascribed, respectively, to the shear thickening and the shear thinning (Muller, 1973) during the irreversible shear breakdown. The shear thickening type showed an abrupt increase in shear stress detected in the increasing shear rate between 66 and 100 s^{-1} . The abrupt increase in shear stress was ascribed to the denser packing condition of the oil droplets occasionally attained with the higher oil ratio of 1.6. This kind of shear thickening

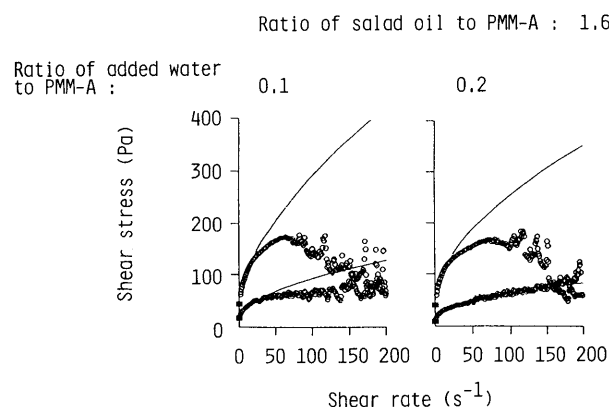


Fig. 3. Different pattern which showed the large loop area in flow curve of fish meat emulsion with high oil ratio of 1.6 prepared from PMM-A.

property (i.e., steeper increase in shear stress in the shear rate range between 20 and 125 s^{-1}) was also detected when typical thixotropy was observed with the addition of more water (ratio 0.2) at an oil ratio of 1.6. A further discussion from a microscopic viewpoint will be made in the following section of this paper.

The hysteresis loop area (Fig. 5) was ascribed to the extent of thixotropy (Muller, 1973) and the irreversible shear breakdown (Nakagawa & Kanbe, 1959). Thixotropy is a reversible structure breakdown during the shear application. When the extent of structure breakdown during the shear becomes large, the flow behavior changes from the thixotropy to the irreversible shear breakdown. In the emulsion prepared from PMM-A, the loop area was 1.55×10^4 $Pa \cdot s^{-1}$ with no added water at an oil ratio of 1.6 and an irreversible shear

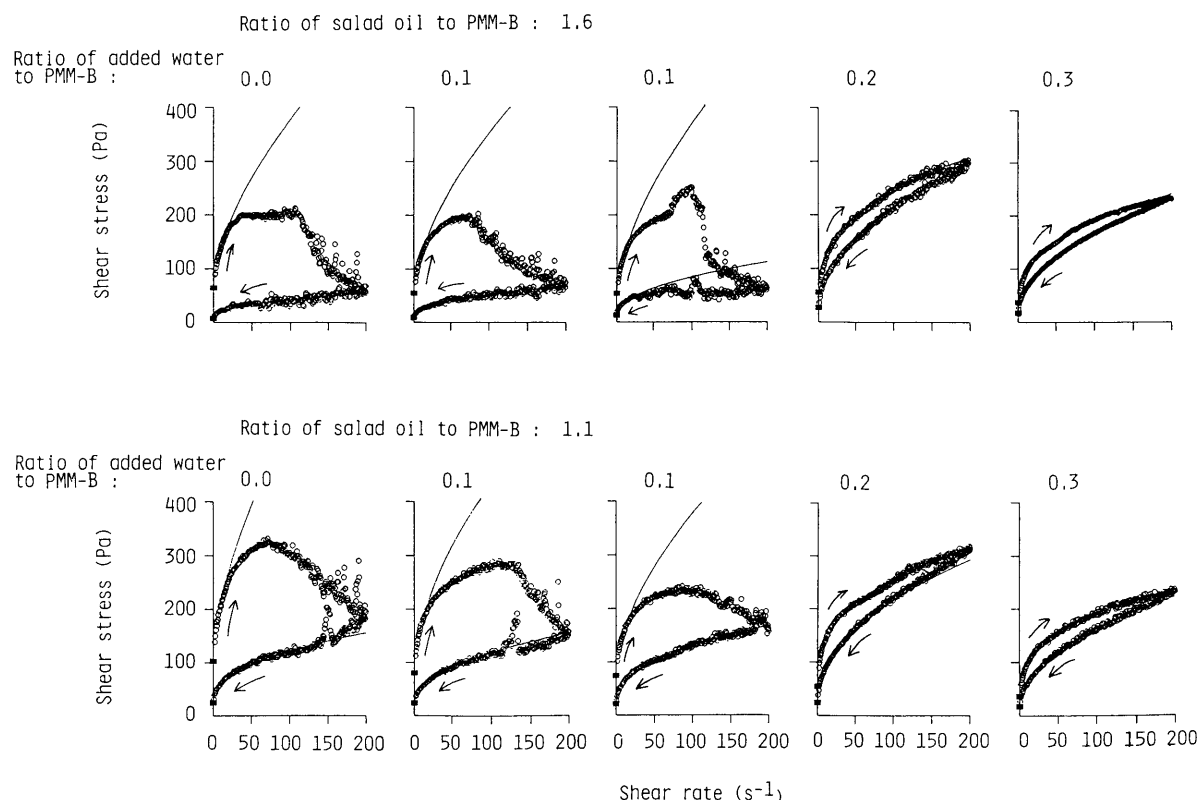


Fig. 4. Effect of added water on flow curve of fish meat emulsion with oil ratios of 1.1 and 1.6 prepared from PMM-B. The arrows along the experimental points indicate an increase or decrease in the shear rate during a continuous experiment.

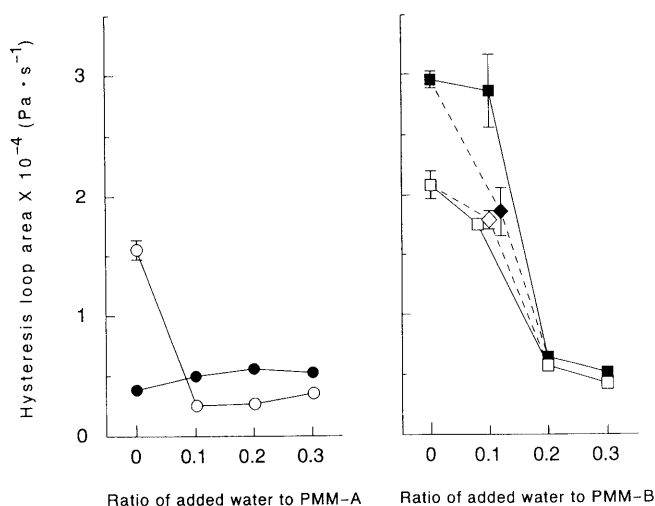


Fig. 5. Effect of added water on hysteresis loop area surrounded by up-curve and down-curve. ●, ■, emulsified product with salad oil ratio of 1.1; ◆, emulsified product with salad oil ratio of 1.1 which showed a moderately large hysteresis loop area as compared with the very large one; ○, □, emulsified product with salad oil ratio of 1.6; ◇, emulsified product with salad oil ratio of 1.6 which showed the shear thickening flow during irreversible breakdown as compared with the shear thinning flow during irreversible breakdown. Symbol with vertical bar indicates mean \pm SD ($n=8$), and the symbols without vertical bar indicate that the sizes of the standard deviation bars ($n=8$) are smaller than the symbol.

breakdown was exhibited. For the other combinations of water and oil ratios, the area was under $0.56 \times 10^4 \text{ Pa} \cdot \text{s}^{-1}$ and the weak thixotropy trend was exhibited. In the emulsion prepared from PMM-B, irrespective of the oil ratio of 1.1 or 1.6, the area was over $1.75 \times 10^4 \text{ Pa} \cdot \text{s}^{-1}$ at the water ratios of

0 and 0.1, and an irreversible breakdown was exhibited. At the water ratios of 0.2 and 0.3, the area was under $0.64 \times 10^4 \text{ Pa} \cdot \text{s}^{-1}$ and a weak thixotropy trend was exhibited.

The addition of water to PMM raised its moisture content. Since the original moisture content of PMM-A and PMM-B was 73.3 and 69.7%, respectively, the addition of 10, 20, and 30% water (i.e., water ratios of 0.1, 0.2, and 0.3) brought about the result that the moisture content of PMM-A became 75.7, 77.8, and 79.5% while the moisture content of PMM-B was 72.5, 74.8, and 76.7%. At an oil ratio of 1.1, irreversible shear breakdown was observed only in the emulsions prepared from PMM-B with the low moisture contents of 69.7 and 72.5%. At an oil ratio of 1.6, irreversible breakdown was observed only in the emulsions prepared from PMM-A with a low moisture content of 73.3% and from PMM-B with low moisture contents of 69.7 and 72.5%. When the moisture content of PMM was increased by the addition of water, the continuous phase of PMM in the emulsion enabled the homogeneous dispersion of oil droplets and the emulsion showed a weak trend of thixotropy instead of irreversible shear breakdown. The increase in the oil phase required more added water to promote the homogeneous dispersion of oil droplets and to prevent the irreversible shear breakdown because it was necessary at a high oil content to increase the amount of the continuous phase and to lower the yield stress and the viscosity at a low shear rate.

The parameters of the power law equation determined by a least-squares method are shown in Fig. 6. In the PMM-A emulsion at the oil ratio of 1.6 with no added water (the left top of the figure), the flow behavior index, n , was the large

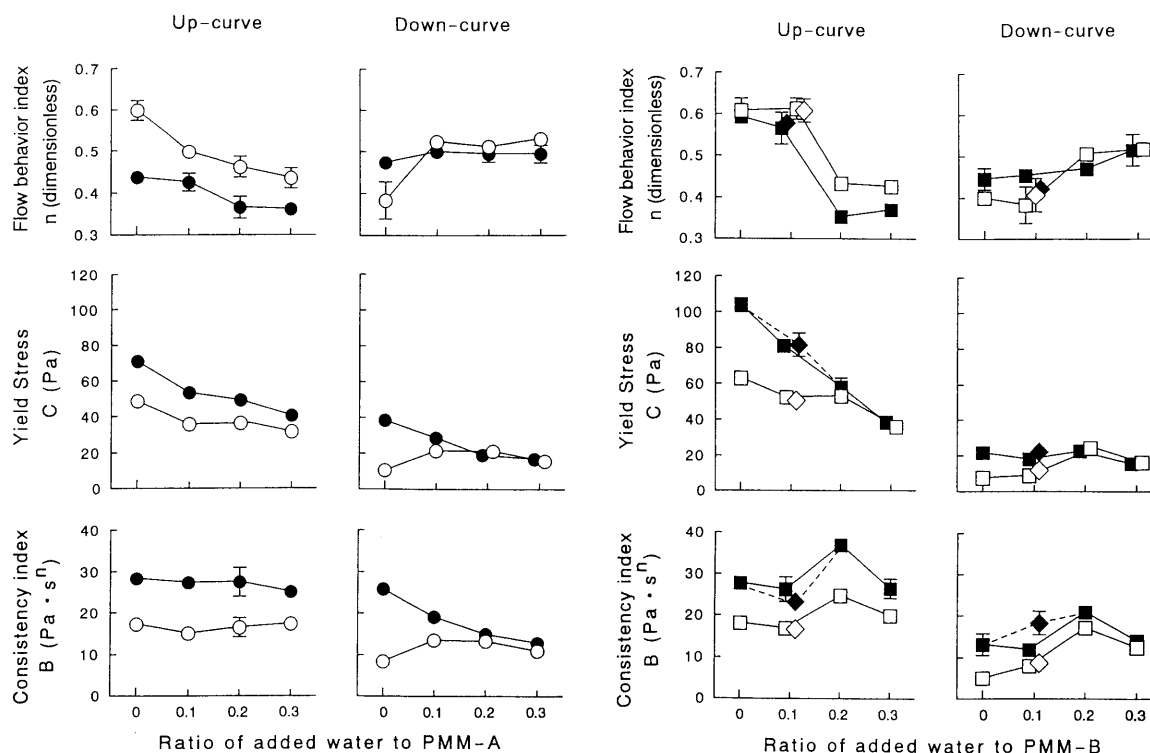


Fig. 6. Effect of added water on rheological parameters obtained from continuous flow curve. ●, ■, emulsified product with salad oil ratio of 1.1; ◆, emulsified product with salad oil ratio of 1.1 which showed the moderately large hysteresis loop area as compared with the very large one; ○, □, emulsified product with salad oil ratio of 1.6; ◇, emulsified product with salad oil ratio of 1.6 which showed the shear thickening flow during irreversible breakdown as compared with the shear thinning flow during irreversible breakdown. Symbol with vertical bar indicates mean \pm SD ($n=8$), and the symbols without vertical bar indicate that the sizes of the standard deviation bars ($n=8$) are smaller than the symbol.

value of 0.60 in the up-curve and the small value of 0.39 in the down-curve. A partial restoration (Nakagawa & Kanbe, 1959) was observed with this small n value in the decreasing shear rates below 20 s^{-1} . Though the shear rate sweep measurement was repeated using the same sample after a rest period of 1 h, a flow curve with more restoration was not obtained during the repetition of increasing shear rate. It was detected by microscopic observation after the first shear rate sweep measurement that the coalescence of oil droplets occurred. During the rest period, the oil separation happened. Therefore, when the shear stress sharply increased at a low shear rate below 20 s^{-1} with a large n value and clearly decreased at higher shear rates above 100 s^{-1} during the increasing shear rate application, it was concluded that irreversible shear breakdown had occurred.

In the other samples of the PMM-A emulsion at an oil ratio 1.1 or 1.6, the n value in the up-curve decreased very gradually from 0.44 to 0.36, or from 0.50 to 0.44 with an increase in added water, and, as the result, the stress at 200 s^{-1} decreased. For these samples, the n value in the down-curve remained almost unchanged around 0.49, or around 0.53, when the amount of added water increased. This n value in the down-curve was larger than the n value in the up-curve, and thixotropy was observed. When the shear rate sweep measurement was repeated using the same sample after the rest period of 1 h, a flow curve with perfect restoration, which was almost the same as the previous one, was obtained.

In the PMM-B emulsions with a water ratio of 0 and 0.1, irrespective of the oil ratio of 1.1 or 1.6 (the right top of the

figure), the flow behavior index n values were over 0.57 in the up-curve and under 0.45 in the down-curve. Since the shear stress sharply increased at low shear rates below 20 s^{-1} with a large n value and clearly decreased at higher shear rates above 100 s^{-1} during the increasing shear, it was concluded that irreversible shear breakdown occurred. Only at the oil ratio of 1.6 with a water ratio of 0 and 0.1, were the n values very small at under 0.41 in the down-curve and partial restoration was observed at the low shear rate below 20 s^{-1} . This result means that irreversible shear breakdown was more remarkable at the oil ratio of 1.6 than at the oil ratio of 1.1 and the stress was not restored at higher shear rates. The occurrence of irreversible shear breakdown was ascribed to the lack of a homogeneous oil droplet dispersion at PMM-B low moisture content. The oil droplets larger than $10 \mu\text{m}$ in diameter were included in the emulsion (Fig. 7).

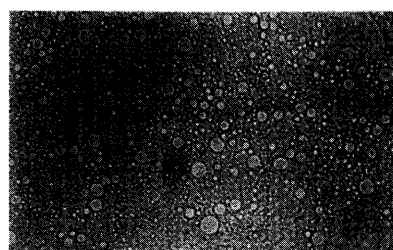
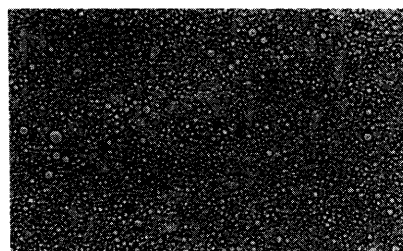
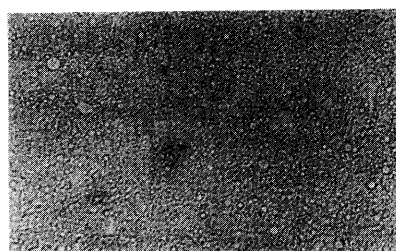
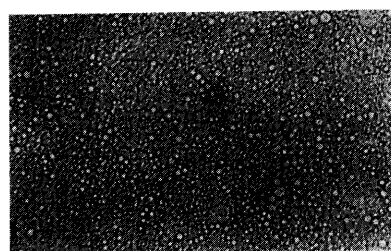
When the water ratio was increased from 0.1 to 0.2 and further to 0.3 in the PMM-B emulsion, the n values in the up-curve significantly decreased and became less than 0.44. With this increase in the water ratio, the n value in the down-curve obviously increased with the oil ratio of 1.6 but only slightly with the oil ratio of 1.1. At the water ratio of 0.3, the n value in the down-curve was almost the same value of about 0.52 irrespective of the oil ratio of 1.1 or 1.6. This n value in the down-curve was larger than the n value in the up-curve, and thixotropy was observed.

In the PMM-A emulsion at an oil ratio of 1.1, the yield stress C decreased from 70 to 42 Pa in the up-curve and from 40 to 17 Pa in the down-curve as the water ratio increased

Emulsifier : EGG-YOLK

Ingredient : PMM-A, salad oil, vinegar

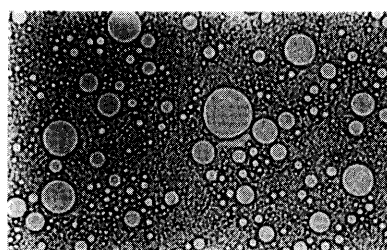
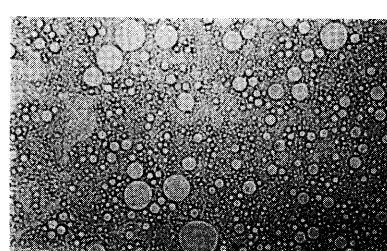
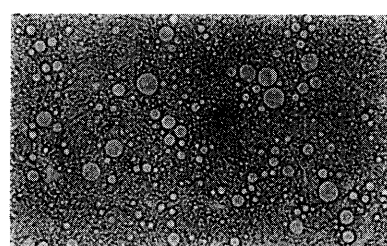
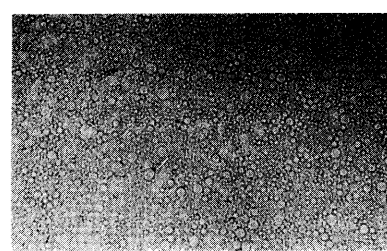
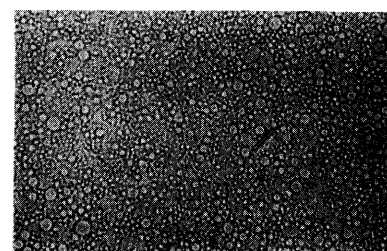
Ratio of salad oil to PMM-A : 1.1

Ratio of added water to PMM-A : 0.0 10 μ mto PMM-A : 0.1 10 μ mto PMM-A : 0.2 10 μ mto PMM-A : 0.3 10 μ m

Emulsifier : EGG-YOLK

Ingredient : PMM-B, salad oil, vinegar

Ratio of salad oil to PMM-B : 1.1

to PMM-B : 0.0 10 μ mto PMM-B : 0.1 10 μ mto PMM-B : 0.1 10 μ mto PMM-B : 0.2 10 μ mto PMM-B : 0.3 10 μ m

Emulsifier : EGG-YOLK

Ingredient : PMM-B, salad oil, vinegar

Ratio of salad oil to PMM-B : 1.6

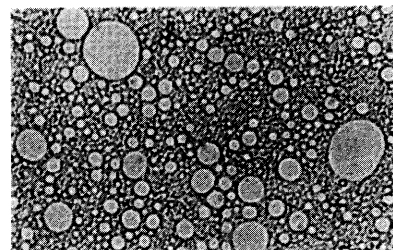
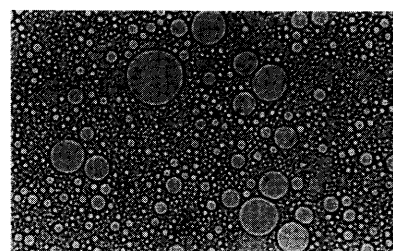
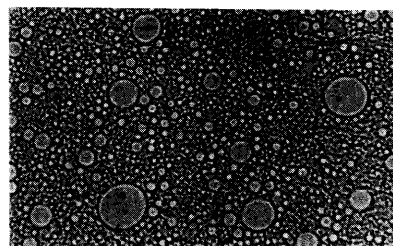
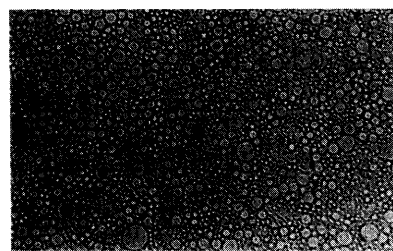
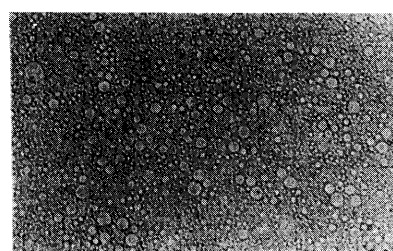
to PMM-B : 0.0 10 μ mto PMM-B : 0.1 10 μ mto PMM-B : 0.1 10 μ mto PMM-B : 0.2 10 μ mto PMM-B : 0.3 10 μ m

Fig. 7. Micrographs of fish meat emulsion with different added water ratios between 0 and 0.3 prepared from PMM-A and PMM-B. In the case of salad oil ratio of 1.1 to PMM-B with added water ratio of 0.1, the upper photograph corresponds to a very large loop area in flow curve while the lower photograph corresponds to a moderately large loop area in flow curve. In the case of salad oil ratio of 1.6 to PMM-B with added water ratio of 0.1, the upper photograph corresponds to the shear thinning flow during irreversible breakdown while the lower photograph corresponds to the shear thickening flow during irreversible breakdown.

from 0 to 0.3 (the left middle of Fig. 6). The difference in the C values obtained from each up-curve and down-curve was found between 25 and 30 Pa when the water ratio increased from 0 to 0.3.

In the PMM-A emulsion at an oil ratio of 1.6 with no added water, the C value in the up-curve was 49 Pa and the value in the down-curve was 11 Pa. The large difference of 38 Pa of these C values was ascribed to the irreversible shear breakdown. With the water ratios of 0.1, 0.2, and 0.3 at an oil ratio of 1.6, the difference in C values in each up-curve and down-curve was small, between 14 and 16 Pa (also refer to Fig. 2). Both the C value itself in the up-curve and the value in the down-curve remained almost unchanged around 37 and 22 Pa, respectively, when the water ratio was increased from 0.1 to 0.2, and slightly decreased when the water ratio was further increased to 0.3. The addition of water at an oil ratio of 1.6 prevented irreversible shear breakdown and brought about the weak trend in thixotropy.

In the PMM-B emulsion at an oil ratio of 1.1, the yield stress C in the up-curve was 104 and 82 Pa with a water ratio of 0 and 0.1, respectively, while it was 58 and 39 Pa with a water ratio of 0.2 and 0.3, respectively. The C value of about 20 Pa in the down-curve, obtained with water ratios of 0 and 0.1, was similar to the value obtained with water ratios of 0.2 and 0.3. The difference in C values in each up-curve and down-curve was large with water ratios of 0 and 0.1, and it was found between 63 and 82 Pa. It was between 23 and 36 Pa with water ratios of 0.2 and 0.3. The large difference with a water ratio of 0 and 0.1 reflected the irreversible shear breakdown.

In the PMM-B emulsion at an oil ratio of 1.6 with no added water, the C value in the up-curve was 65 Pa and the value in the down-curve was 8 Pa. When the water ratio was increased to 0.1, the C value in the up-curve decreased slightly to 54 Pa but the value in the down-curve was still small at around 10 Pa. The difference in C values in each up-curve and down-curve was large for water ratios of 0 and 0.1, and it was between 44 and 57 Pa. This large difference with these water ratios reflected the irreversible shear breakdown. When the water ratio was increased from 0.1 to 0.2, the C value in the up-curve remained unchanged but the value in the down-curve increased to 25 Pa. When the water ratio was further increased to 0.3, the C values in both the up-curve and the down-curve decreased. The difference in C values in each up-curve and down-curve became small with water ratios of 0.2 and 0.3, and it was between 21 and 29 Pa. This small difference with these water ratios reflected the weak trend in thixotropy.

In the PMM-A emulsion, irrespective of the oil ratio of 1.1 or 1.6, the consistency index B in the up-curve remained almost unchanged between 25 and 28 Pa·s^{*n*} with a low oil ratio, or between 15 and 18 Pa·s^{*n*} with a high oil ratio, when the water ratio was increased (the left bottom of Fig. 6). At the oil ratio of 1.1, the B value in the down-curve decreased from 26 to 13 Pa·s^{*n*} thus getting softer consistency as the water ratio was increased. At the oil ratio of 1.6, the B value in the down-curve was low at around 9 Pa·s^{*n*} with no added water because of the irreversible shear breakdown, and increased to about 14 Pa·s^{*n*} with the addition of water due to the weak

trend in thixotropy.

In the PMM-B emulsion, irrespective of the oil ratio of 1.1 or 1.6, the B value in the up-curve increased with the water ratio of 0.2 and decreased with the water ratio of 0.3. This change in B value is related to the combination of both the B and n values. At water ratios of 0 and 0.1, the B value in the up-curve was small at around 27 Pa·s^{*n*} with low oil ratios, or around 18 Pa·s^{*n*} with high oil ratios, and the n value was large (refer to the previous paragraph). When the water ratio was increased to 0.2, the B value in the up-curve became large at around 37 Pa·s^{*n*} with a low oil ratio, or around 25 Pa·s^{*n*} with a high oil ratio, and the n value became small. As a result, the curve drawn by the power law equation became less linear at a water ratio of 0.2, and the experimental data in the increasing shear rate range between 20 and 200 s⁻¹ also existed on this curve. This result means that the flow behavior changed from an irreversible shear breakdown to a weak thixotropy trend when the water ratio was increased from 0.1 to 0.2. In the down-curve, both the B and n values were small with water ratios of 0 and 0.1 due to the irreversible shear breakdown, and became large with water ratios of 0.2 and 0.3 due to the weak thixotropy trend. In the PMM-B emulsion with the water ratios of 0 and 0.1, the larger shear stress was generated under both the increasing and decreasing shear rate applications below 20 s⁻¹ at an oil ratio of 1.1 than at the oil ratio of 1.6 (Fig. 4) because, in addition to the similar high n value, a higher B value due to higher friction was induced by smaller and more uniform oil droplets (Fig. 7).

In the PMM-A emulsion with any water ratio, the B and C values in the up-curve were higher and the n value was lower at the oil ratio of 1.1 than at the ratio of 1.6. The emulsion with an oil ratio of 1.1 was characterized by a higher viscosity at low shear rate with higher B and C values and more shear-thinning consistency with a lower n value (also refer to Fig. 2).

Difference in oil droplet size of fish meat emulsion with the addition of water The microstructure of fish meat emulsions is shown in Fig. 7. As the water ratio was increased irrespective of the PMM-A emulsions or PMM-B emulsions, the size of the oil droplets became smaller.

In the PMM-A emulsion at an oil ratio of 1.1 irrespective of the water ratio between 0 and 0.3, the small size oil droplets were uniformly dispersed. The modal diameter (droplet size most frequently seen: Arakawa, 1977) was 1.5 μm even with no added water and 0.5 μm at a water ratio of 0.1. The extremely small particles on the background in the micrograph of Fig. 7 were the oil droplets with modal diameter. These modal diameters were reconfirmed by scanning electron microscopy (Nakayama & Tomita, 1996).

In the PMM-B emulsion with water ratios of 0 and 0.1, the large oil droplets were remarkably dispersed. When the water ratio was increased to 0.2 and 0.3, the size of the oil droplets became smaller and a uniformly dispersed emulsion was prepared.

In the PMM-B emulsion with a water ratio of 0.1 irrespective of the oil ratio of 1.1 or 1.6, some samples showed typical irreversible shear breakdown, while other samples showed the flow property which was defined between the breakdown and thixotropy. On the whole, this emulsion was

in the intermediate state. At the oil ratio of 1.1, the large size oil droplets between $3.3\ \mu\text{m}$ and $20\ \mu\text{m}$ which were dispersed together with the oil droplets of modal diameter $2.3\ \mu\text{m}$ corresponded to the very large loop area in the flow curve, and the oil droplets between $3.3\ \mu\text{m}$ and $10\ \mu\text{m}$, which were dispersed together with the droplets having a modal diameter of $2.3\ \mu\text{m}$, corresponded to the moderately large loop area. At the oil ratio of 1.6, the large size oil droplets between $5.0\ \mu\text{m}$ and $27\ \mu\text{m}$, which were dispersed together with the droplets having a modal diameter of $3.3\ \mu\text{m}$, corresponded to the shear thinning flow during irreversible breakdown, and the oil droplets between $5.0\ \mu\text{m}$ and $20\ \mu\text{m}$, which were dispersed together with the droplets having a modal diameter $3.3\ \mu\text{m}$, corresponded to the shear thickening flow during irreversible breakdown.

With the water ratio of 0.2 at an oil ratio of 1.1, the modal diameter became $1.0\ \mu\text{m}$ and oil droplets of uniform size were dispersed. The small loop area was exhibited due to the weak thixotropy trend. With the water ratio of 0.2 at an oil ratio of 1.6, the modal diameter became $1.5\ \mu\text{m}$ and oil droplets of uniform size were dispersed. A small loop area was also exhibited due to the weak thixotropy trend.

The following conclusion was drawn with respect to the effect of added water. When the amount of added water to PMM was increased, the flow behavior changed from the irreversible shear breakdown to the weak trend in thixotropy and a small loop area was exhibited. The decrease in loop area was ascribed to the softer and easily flowing consistency with a small n value below 0.50 in the up-curve given by the increase in moisture content. This thixotropic and softer consistency enabled the dispersion of oil droplets which were small and uniform in size. At the high oil content with the addition of water, a shear thickening flow was exhibited in the irreversible breakdown due to the denser packing condition of oil droplets occasionally attained. This kind of shear thickening property was also detected when typical thixotropy was observed with the addition of more water at the high oil content.

When compared at the oil ratio of 1.1 with regard to the same water ratio, the size of the oil droplets was smaller in the PMM-A emulsion than in the PMM-B emulsion. In the PMM-B emulsion, the size of the oil droplets was smaller at the oil ratio of 1.1 than at the oil ratio of 1.6.

PMM-A was emulsified even with no added water. The emulsification of PMM-B required the addition of 20% water. When the oil ratio was increased from 1.1 to 1.6, the emulsion prepared from PMM-A became unstable during the shear application and also during storage. The stability of the PMM-B emulsion remained almost unchanged with an increase in oil content. PMM-A was superior to PMM-B in its emulsifying ability but was of narrow application from the viewpoint of the maximum permissible amount of the oil phase.

When the amount of added water to PMM was zero or little, the yield stress and the viscosity at a low shear rate were large. As a result, the homogeneous dispersion was disturbed and the oil droplets tended to coalesce. In this condition, the large oil droplets were included in the fish meat emulsion. When the amount of added water was increased and the softer

and an easier flowing consistency was given to the PMM matrix, small sized oil droplets were uniformly dispersed.

The instability of the PMM-A emulsion with the high oil ratio of 1.6 was discussed. PMM-A was prepared through the process of grinding in weak alkaline solution while suspension in the same solution was carried out for the preparation of PMM-B. In this process, PMM-A was fragmented into much shorter myofibrils than PMM-B (Nonaka *et al.*, 1989). As a result, when the homogenization was carried out using the Polytron for the emulsion preparation, the PMM-A emulsion included much smaller myofibril fragments than the PMM-B emulsion. The finer network structure of filaments, each approximately 35 nm in diameter, unbundled from the myofibrils, was found in the PMM-A emulsion (Nakayama & Tomita, 1996). Therefore, the small $0.5\ \mu\text{m}$ diameter oil droplets were initially dispersed. When the oil content was high (ratio 1.6), the small size oil droplets could not be retained for a long time in such a fine network structure, and were soon followed by coalescence. This is the reason for the storage instability of the PMM-A emulsion with a high oil content, and the microscopic presentation of this emulsion was impossible because the droplet size changed by the minute.

References

- Arakawa, M. (1977). Electron microscopic observation of particle size. In "Lecture on New Experimental Chemistry, Vol. 18, Interface and Colloid," 1st ed., ed. by Chemical Society of Japan. Maruzen, Tokyo, p. 383.
- Muller, H. G. (1973). "An Introduction to Food Rheology," 1st ed., Crane, Russak & Company, Inc., New York, pp. 59-74.
- Nakagawa, T. and Kanbe, H. (1959). Shear stability, thixotropy, and irreversible shear breakdown. In "Rheology," 1st ed., Misuzu Shobou, Tokyo, pp. 456-462.
- Nakayama, T. and Tomita, H. (1996). Microstructure of fish meat emulsion with addition of egg-yolk. Presented at the 43rd Annual Conference of the Japanese Society for Food Science and Technology, Sendai, March 28-30, p. 132.
- Nakayama, T., Oka, T., Ooi, A., Nonaka, M., Hirata, F. and Saeki, H. (1992). New emulsified product from sardine meat preparation with very low lipid content. *Nippon Shokuhin Kogyo Gakkaishi*, **39**, 451-456.
- Nakayama, T., Tozaki, Y., Wakabayashi, A. and Ooi, A. (1993a). Effect of yolk and white on shear-stable emulsion preparation from fish. *Nippon Shokuhin Kogyo Gakkaishi*, **40**, 194-204.
- Nakayama, T., Wakabayashi, A., Tozaki, Y. and Ooi, A. (1993b). Different effects of whole egg and egg-yolk on emulsion preparation from a fish meat product. *Nippon Shokuhin Kogyo Gakkaishi*, **40**, 872-880.
- Nakayama, T., Tomita, H., Murase, M. and Ooi, A. (1994). Effect of added water amount and yolk white ratio on flow property of fish emulsion. Presented at the 41st Annual Conference of the Japanese Society for Food Science and Technology, Tokyo, March 28-30, p. 128.
- Nakayama, T., Tomita, H. and Ooi, A. (1995). Relationship between change in flow property and coalescence of oil droplets in fish meat emulsion with addition of egg-white. *Food Sci. Technol., Int.*, **1**, 82-88.
- Nonaka, M. (1990). Pulverization in water. In "The Nutritive Components of Fish and New Fish Utilization Technology," 1st ed., ed. by M. Takeuchi. Kouseisha-Kouseikaku, Tokyo, pp. 88-95.
- Nonaka, M., Hirata, F., Saeki, H. and Sasamoto, Y. (1989). Manufacture of highly nutritional fish meat for food stuff from sardines. *Nippon Suisan Gakkaishi*, **55**, 1575-1581 (in Japanese).