Asian Fisheries Science **9** (1996): 153-160.
Asian Fisheries Society, Manila, Philippines
https://doi.org/10.33997/j.afs.1996.9.3.001

Degradation of Chlorophyll in Dried Wakame *(Undaria pinnatifida)* During Storage

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Abstract

The storage condition of dried wakame, which contained 57.9% alginate, with a D-mannuronic acid to L-guluronic acid ratio of 1.92, was investigated. The water sorption isotherms of dried wakame and sodium alginate qualitatively resembled each other, but showed slight quantitative differences above A_w 0.70. The amounts of water sorbed in a monomolecular layer of dried wakame and sodium alginate were 4.4 and 5.1 (g $H_2O \cdot 100\ g^{-1}$ solids), respectively. It was suggested from the results obtained in this study that the water adsorption of dried wakame was attributable to the presence of alginate, the main structural component of wakame.

From the differential scanning calorimetry (DSC) thermograms of dried wakame and sodium alginate, only a single endothermic peak was observed between 20 and 90°C for both samples. The endothermic peak temperatures decreased linearly with increasing water activity. The degradation of chlorophyll followed pseudo-first order reaction. The rates of chlorophyll degradation profoundly faster above the DSC endothermic peak temperature of wakame compared with those below the endothermic peak temperature, suggesting that the stability of chlorophyll in wakame depends largely upon the state of alginate.

Introduction

Wakame, *Undaria pinnatifida* (Harvey), is one of the most popular seaweeds consumed as food in Japan. The cultivation of wakame began around 1940 and reached full-scale production after 1955 (Yamanaka and Akiyama 1993). With consumers becoming more health conscious, there has been a trend toward foods with reduced salt, fat, cholesterol and calories, as well as increased dietary fiber and vitamins. Therefore, the consumption of wakame in Japan has been constantly increasing owing to its high dietary fiber content.

On the other hand, since the quality of wakame decreases quickly after harvest, such techniques as drying, mixing with ash, salting, boiling and soaking in acid solution to preserve wakame have been traditionally developed (Sato et al. 1976; Watanabe and Nishizawa 1982; Shiba et al. 1984; Yamanaka and Akiyama 1993). Because of consumer preference for bright-green wakame, large quantities of wakame are nowadays processed as so-called "cut wakame" in Japanese factories. The boiled and salted wakame prepared immediately after harvest is washed, chopped, desalted and dried mechanically (Yamanaka and Akiyama 1993). Storage conditions of dried seaweed products, such as wakame, nori (*Porphyra yezoensis*) and kombu (*Laminaria japonica*), have been evaluated mostly from the standpoint of water content, water activity, storage temperature and environmental humidity (Jensen 1969; Hirata et al. 1984; Hirata and Ishitani 1985).

In this study, the change of chlorophyll content in dried wakame as an index of quality during storage was determined, and its storage condition was discussed from the differential scanning calorimetry (DSC) endothermic peak temperature of alginate, the main component of dried wakame.

Materials and Methods

Samples

Dried wakame used in this study was obtained from Marutsune Co., Ltd. in Shizouka Prefecture, Japan. According to the company's production procedure, wakame was boiled after harvest and stored in salt. After desalting, wakame was mechanically dried. Dried wakame was mechanically ground to a 100 mesh size in our laboratory. Sodium alginate (300-400 cP) was purchased from Wako Pure Chemical Ind., Ltd. (Tokyo, Japan).

Storage Conditions

Water activities (A_w) of powdered wakame and sodium alginate were adjusted by keeping them for the appropriate period at 25°C with desiccators containing saturated salt solutions which give different A_w. Saturated salt solutions employed in this study were diphosphorus pentaoxide (A_w 0.00), sodium hydroxide (A_w 0.07), lithium chloride (A_w 0.11), potassium acetate (A_w 0.23), magnesium chloride (A_w 0.33), potassium carbonate (A_w 0.42), magnesium nitrate (A_w 0.52), sodium bromide (A_w 0.58), sodium nitrite (A_w 0.66), sodium chloride (A_w 0.75), potassium chloride (A_w 0.86) and potassium nitrate (A_w 0.93; Rockland 1960). Dried wakame with different water activities were stored in hermetically sealed glass containers at 30-80°C for up to 20 d in the dark.

Differential Scanning Calorimetry (DSC)

DSC was conducted in a Perkin-Elmer DSC-7 equipped with an Intracooler (Perkin-Elmer Co., Norwalk, CT, USA). Powdered wakame or sodium alginate was hermetically sealed in aluminium sample pans (Perkin-Elmer No. 219-0062) and thermally scanned at 5°C•minute^{-1} over 20-90°C. The instrument was temperature-calibrated using indium (m.p. 156.60°C). The endothermic peak temperatures were determined with data analysis programs supplied by Perkin-Elmer. An empty sealed pan was used as reference.

Determination of Chlorophyll

The amount of chlorophyll in dried wakame was determined according to the procedure reported by Hirata et al. (1981).

Results and Discussion

Water Sorption Isotherm

The content of alginate in dried wakame used in this study was found to be 57.9%, which agrees with data reported previously (Saito et al. 1987). D-mannuronic acid to L-guluronic acid ratios of dried wakame and sodium alginate were 1.92 and 3.48, respectively.

Water sorption isotherms of powdered wakame and sodium alginate were obtained at 25°C. These isotherms are presented in Fig. 1. The isotherms obtained are qualitatively similar between wakame and sodium alginate, but show some quantitative differences above A_w 0.7. At any given water activity, the moisture content of wakame was higher than sodium alginate at the range of water activity above 0.7. It can be concluded that the slight sigmoid shape of the first part of the isotherms in Fig. 1 is caused by the water sorption of alginate; and the sharp increase in water content at higher water activities may be due to free sugars present in wakame (Nishide et al. 1988).

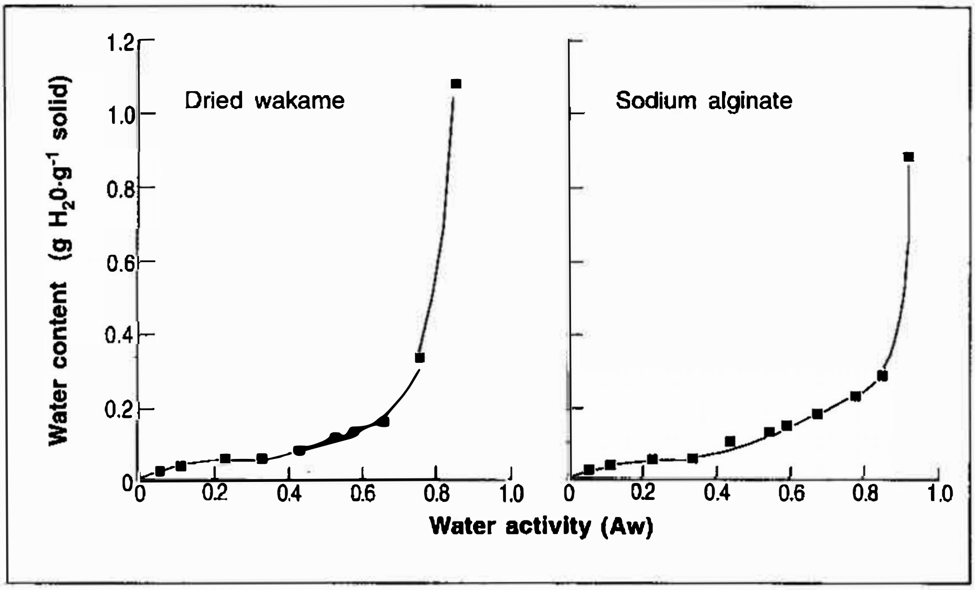

Fig. 1. Water adsorption isotherms of dried wakame and sodium alginate at 25°C.

To calculate the amount of water held by powdered wakame or sodium alginate in a monomolecular layer, the B.E.T. equation was used (Brunauer et al. 1938). The amounts of water sorbed in a monomolecular layer (g water•100 g^{-1} solids) of wakame and sodium alginate were 4.4 and 5.1, respectively. The monolayer values of wakame and sodium alginate correspond to A_w's of 0.16 and 0.17, respectively. Since the monolayer value of food gives a good estimate of the water content that provides maximum stability of a dry product, this value is of considerable practical importance (Karel and Nickerson 1964). The inflection points of the isotherm curves, which indicate transitions from one type of water adsorption to another, were observed at A_w's 0.23, 0.34 and 0.73 for wakame; and at A_w's 0.20, 0.37 and 0.81 for sodium alginate. From these results, it is suggested that adsorption of water by dried wakame is attributed to the presence of alginate, the main component of wakame.

Differential Scanning Calorimetry

DSC thermograms of dried wakame and sodium alginate had the characteristic profile shown in Fig. 2. Only a single endothermic peak (enthalpic peak) was observed in the range of 20-90°C for both samples. The endothermic peak temperatures of wakame and sodium alginate decreased linearly with increasing water activity as presented in Fig. 3, although sodium alginate had lower endothermic peak temperatures at equal water activities. The overall decreasing pattern of endothermic peak temperature of wakame against water activity was similar to that for sodium alginate (Fig. 3). The decrease of endothermic peak temperature could be typical of materials plasticized by water (Roos and Himberg 1994).

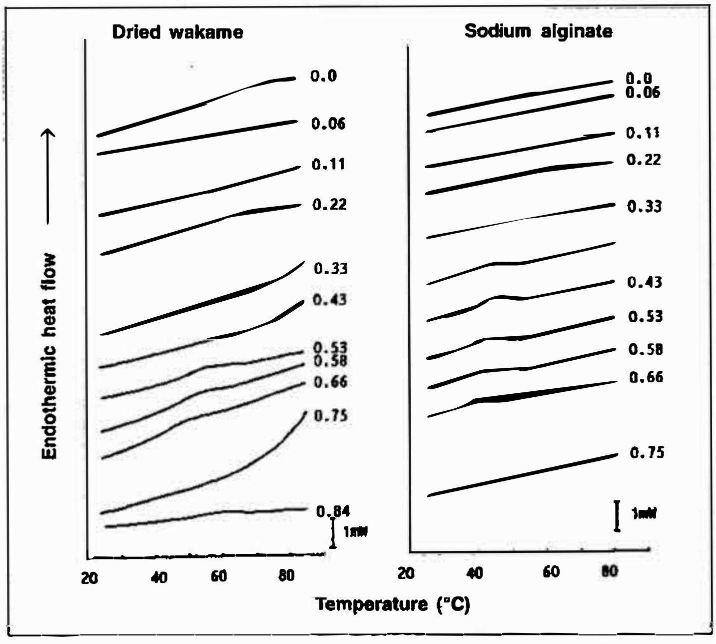

Fig. 2. DSC thermograms of dried wakame and sodium alginate.

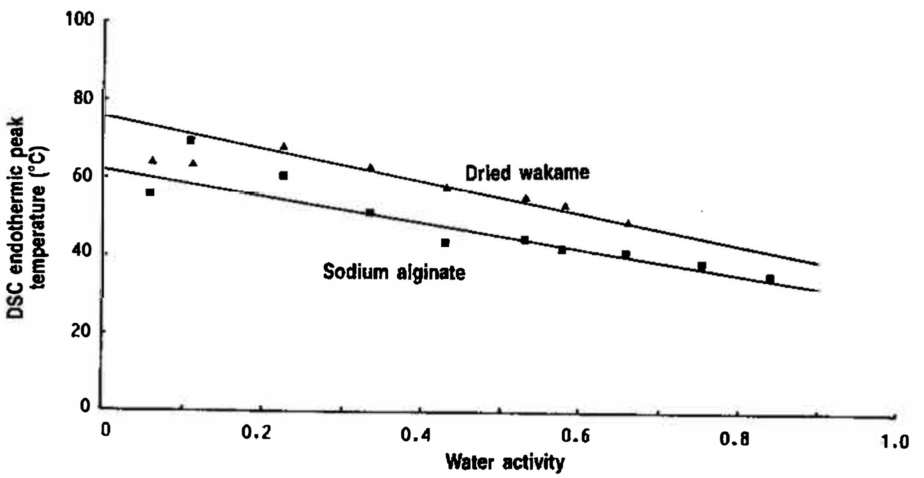

Fig. 3. Effect of water activity on the DSC endothermic peak temperatures of dried wakame and sodium alginate.

From these results, it is clear that the endothermic peak temperature observed in wakame might be due to some structural or chemical changes of alginate contained in wakame.

Degradation of Chlorophyll in Wakame During Storage

Wakame powders with A_w's 0.22, 0.44, 0.53 and 0.66 were hermetically sealed and stored at four different temperatures for up to 20 d. Two storage temperatures were set higher than the DSC endothermic peak temperature of the sample, and the rest were below the endothermic peak temperature. Fig. 4 depicts the degradation of wakame chlorophyll during storage. The color of dried wakame changed rapidly during storage from bright-green to olive-brown, which is characteristic of pheophytin, the degradation product of chlorophyll. It is obvious from Fig. 4 that water activity significantly influenced the degradation rate of chlorophyll in dried wakame, and the degradation pattern of chlorophyll followed the pseudo-first order reaction during the initial stage of storage. For the samples with lower A_w's, chlorophyll degradation was slow, suggesting that chlorophyll is strongly bound in nonreactive compartments or that water is not available for the degradation (LaJolo et al. 1971). These findings are in general agreement with data reported on freeze-dried spinach purée (Gupte et al. 1964; LaJolo et al. 1971; LaJolo and Marquez 1982).

The rates of chlorophyll degradation were profoundly faster in storage temperatures above the DSC endothermic peak temperature of wakame compared with those below the endothermic peak temperature. This phenomenon was clearly elucidated by the Arrhenius plots for the degradation of total chlorophyll in dried wakame (Fig. 5), where the logarithm of the degradation rate is plotted as a function of the reciprocal of the absolute temperature. It appears from this analysis that there are sharp breaks in the curves relating rates

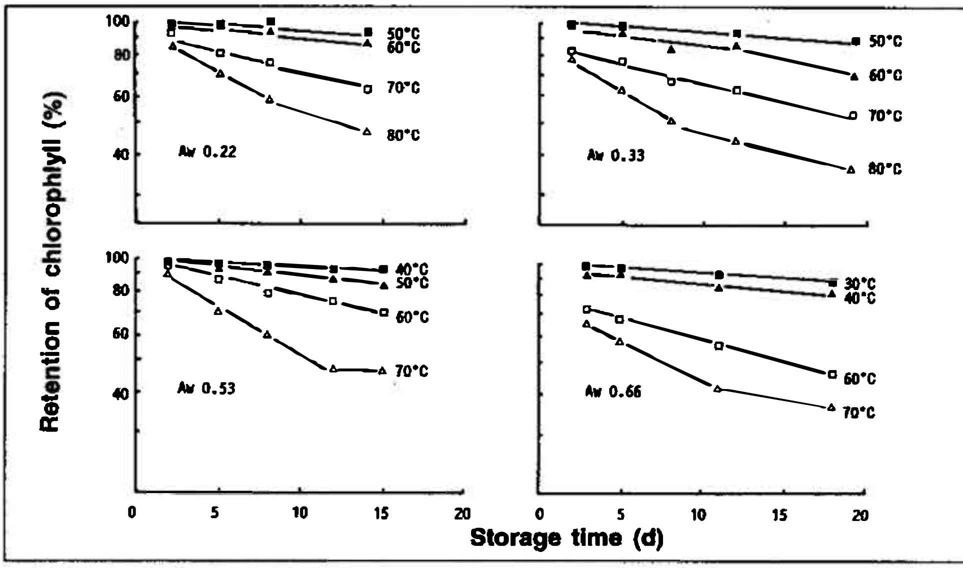

Fig. 4. Effect of water activity and storage temperature on the degradation of chlorophyll in dried wakame.

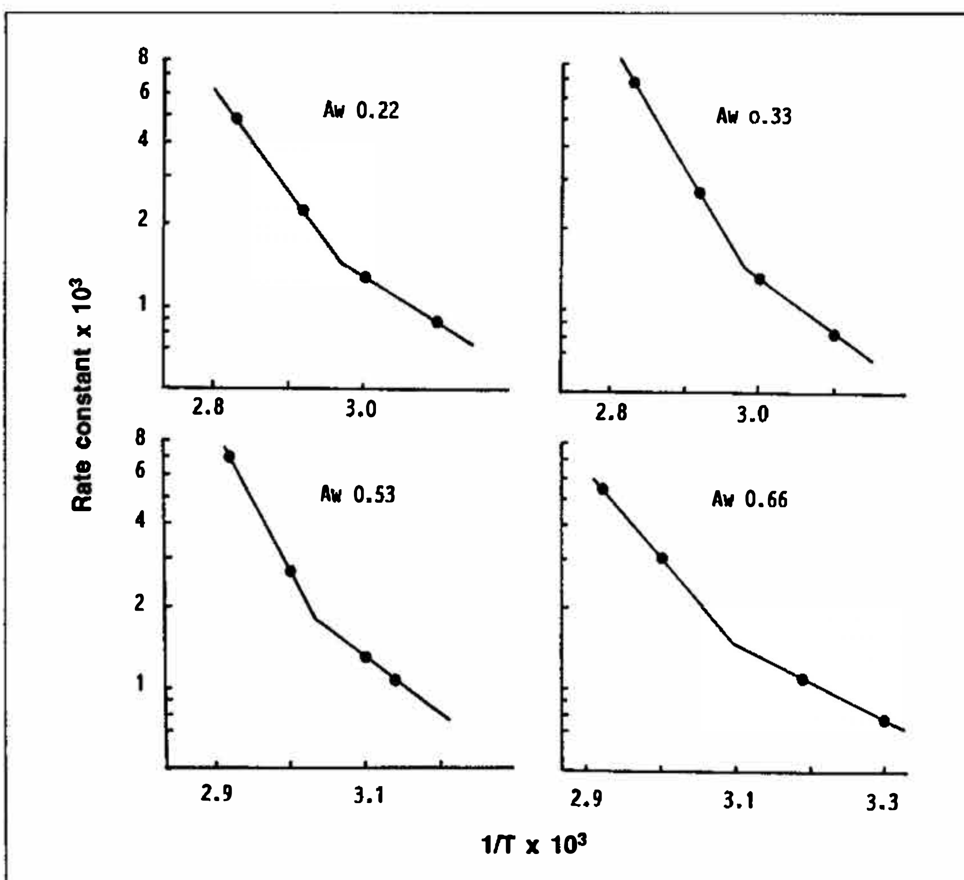

Fig. 5. Arrhenius plots for the degradation of chlorophyll in dried wakame.

of chlorophyll degradation with storage temperature. Temperatures corresponding to the inflection points of the Arrhenius plots were 63.4°C (A_w 0.22), 62.2°C (A_w 0.33), 56.6°C (A_w 0.53) and 50.0°C (A_w 0.66), while the DSC endothermic peak temperatures of dried wakame (Fig. 2) were 67.6°C (A_w 0.22), 62.4°C (A_w 0.33), 55.2°C (A_w 0.53) and 49.0°C (A_w 0.66). It is apparent from these results that the inflection temperatures of the Arrhenius plots coincide with the DSC endothermic peak temperatures. This suggests that the stability of chlorophyll in wakame is largely dependent on the state of alginate, since alginate is the main structural component of wakame, and the DSC endothermic peak temperatures of alginates are close to those of dried wakame.

In conclusion, storing dried wakame below the DSC endothermic peak temperature is recommended from the results of this study. Therefore, the determination of water content or water activity of products is not required to predict the shelf-life of dried wakame. Further study on the relationship between the state of alginate in dried wakame and the degradation rate of chlorophyll is now in progress in our laboratory.

Acknowledgment

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (No. 06660261).

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Manuscript received 5 April 1995; accepted 7 June 1996.