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Existence of gel-glasslike transition point in biopolymer gels[1]

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Abstract

The existence of a gel-glasslike transition point in biopolymer gels such as egg-white is demonstrated with the consideration of the competitions of the free and the bound waters of gel, and a possible existence of the similar transition points are suggested for DNA gel, ribosome RNA/DNA mixtures gel, gelatin gel, agarose gel, konjak gel, and others. The time variations of the weight during the desiccation process of egg-white gel and several other gels were measured to be revealed as two or more stages. It is verified by the time domain reflectometry method (TDR) that the first and second stages are attributed to the lose of the free and bound water in the egg-white gel, respectively. The existence of gel-glasslike transition point may be a common phenomenon for materials in which the molecular network contains free and bound waters. © 1998 Published by Elsevier Science B.V.

The boiled egg-white is known as one of the most popular biological gels. Recently, it has been reported that the turbid boiled egg-white became glass-like state in the dry atmosphere (5°C, 1 atm) [1]. In this process, the opaque specimen turns transparent (light yellow colored). The simple vitrification method of denatured proteins such as egg-white which had become opaque by boiling has been carried out. In this study, the vitrification is defined as follows: the material has glass transition (Differential Thermal Analysis (DTA) study showed a distinct endothermic peak due to the transition [2], and the peak position was located at 36, 42, 58 and 69°C when the heating rates were 2, 5, 10, and 20°C/min, respectively), and become transparent under visible light, amorphous characteristics of X-ray diffraction halo-pattern and rigidity as a common glass. The vitrified solid which was obtained from egg-white had such characteristics. We verified the above mechanism by measuring the dielectric relaxation time of water in gel by the technique of the time domain reflectometry (TDR).

The vitrification of the denatured biogels was very simple: it was done simply by keeping the boiled opaque egg-white in a refrigerator (5°C, 1 atm) or a drying equipment (25°C, 1 atm, humidity 36%) after the shell and the hardened egg yolk were removed in order to vapor out the moisture. As early as a day after refrigeration, the thin edge which was elastic began to harden and became transparent. The weight was reduced by 30% after 60 h as shown in the Fig. 1 and most of it, except the thick parts, hardened and became transparent. When the weight became about 17% of the first weight, all the egg-white hardened perfectly and vitrified (gel-glasslike transition: transition point 17%). This result shows the existence of the transition of two states during the drying process for

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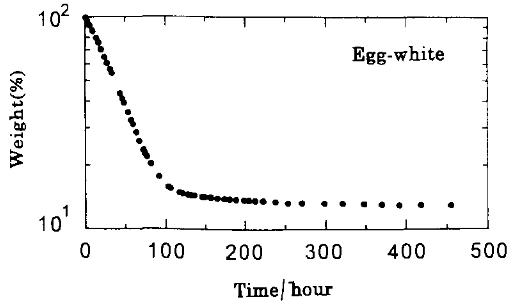

Fig. 1. Gel-glasslike transition: Two stages of moisture evaporation in boiled egg-white kept in an ordinary drying equipment (5°C, 1 bar; refrigerator) and the state of its transparency. Ordinate, weight reduction of boiled egg-white. The thin edges of boiled egg-white became hard and transparent (vitrified) after about 100 h. Finally, after about 200 h, all the egg-white was hard and transparent like glass.

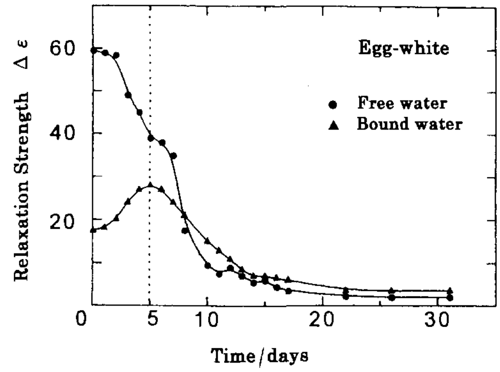

Fig. 2. Variation of dielectric relaxation strength $\Delta\varepsilon$ with the drying time for a egg-white measured by a TDR at 25°C. Each value of the free and bound waters is obtained by the result of measuring of the frequency dependence of dielectric dispersion (ε') and dielectric absorption (log ε'') for egg-white. The intensity of two dielectric relaxation peaks were found in egg-white due to the free and bound waters responding to the frequencies of the microwave around 10^{10} Hz and 10^8 Hz, respectively.

gel. As shown in the Fig. 1, the evaporation of the moisture from the boiled egg-white was seen in two stages. The evaporation rate in the first stage was much higher than that of the second one. The first stage evaporation continued until the weight was reduced to about 20% of the first weight at which point it entered the second stage, which continued until all the water content of the egg-white, 88%, had evaporated. As the two stages of the evaporation are so different, the moisture vapored out at the first stage might be considered to be the water weakly bound to the proteins, namely, the free water, and that of second stage, to be the strongly bound to the proteins, namely, the bound water [3,4] (Fig. 2).

About 40 proteins contain in the egg-white are known, and considering the molecular weight of the proteins among them and neglecting the other proteins because of their small constituents we could estimate 51,000 daltons for the average molecular weight at the proteins. The contents of the free and bound water were estimated as 19,000 and 1,900 mol per 1 mol of the protein in the egg-white, respectively, from the above results. In other words, 1 g of proteins contained 7 g of the free water and 0.7 g of the bound water. Assuming that average molecular weight of amino acids is 110 daltons, it could be computed that one amino acid contains 40 and 4 mol of the free and bound water, respectively.

Heat treatment of vitreous egg-white at 60°C or γ-ray irradiation resulted in partial crystallization, and the XRD patterns showed a few diffraction peaks superimposed on the halo peak due to the glassy phase [2].

Finally, we wish to suggest that the existence of similar gel-glasslike transition points are able to be observed clearly in DNA gel, gelatin gel, agarose gel and others during the drying process. This phenomenon is occurred in several biogels (ribosome RNA/DNA mixtures, tofu, konjak), foods (dried bonito, boiled fishpaste, green vegetables, radish, carrot), fruits (pear) and moist papers.

In conclusion, the existence of the gel-glasslike transition point may be a common phenomenon for materials in which the molecular network contains free and bound waters and the positions of the transition points are originated from the competitions of the free and bound waters involved.

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