Thermal Behavior of Albumin Gel in Low Water Content

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In the differential scanning calorimetry (DSC), it was found that the transition behavior of egg-white gel is complicated in low water contents \( w_c = \frac{w_{\text{water}}}{w_{\text{dried gel}}} \) ranging from 0.1 to 1.8. The thermogram shows a glass transition and peaks related to the melting and recrystallization of water. In the present study, the sol-gel transition behavior of albumin of chicken egg in low water contents \( w_c = 0.19-3.24 \) was studied by DSC. Moreover, the thermal behaviors of the gels were intensively studied. In a sol-gel transition process, four endothermic peaks were observed. The peak temperatures are increased as the water content \( w_c \) is reduced \((w_c < 1)\). The thermal behavior of albumin gel showed complicated behavior similar to the egg-white gel. Amount of free water (which is frozen at 0 °C) in the gel is estimated from the thermogram.

Key words: albumin, egg-white, low water content, sol-gel transition, differential scanning calorimetry, free water

1. INTRODUCTION

Gel shows peculiar properties, such as the volume phase transition [1], by changing the interaction of polymer network and solvent. Therefore, it is very interesting how the gel behaves when the solvent is going to disappear. Since the first report on gel-to-glasslike transition in egg-white gel dehydration by Takushi et al. [2], extensive investigations on the property changes in the transition have been carried out [3-5]. It is one of the characteristic features during the dehydration process of the gel that the log weight shows a decrease proportional to the dehydration time and the slope alters at a certain time \( t'_{g} \) [2]. The linear behavior with a steep slope in the early stage of the dehydration process before \( t'_{g} \) is due to the loss of free water, while, that with a gentle slope after \( t'_{g} \) results from the loss of bound water.

Besides, with increasing temperature, the dehydrated gel shows the characteristic features in differential thermal analysis, which is similar to usual glass transition [6]. Polyacrylamide (PAAm) gel, which is one of the most popular synthesized gels with simpler composition than egg-white gel, also becomes hard and transparent upon dehydration. The characteristic phenomena were revealed by examining the time dependence of elastic stiffness during the dehydration processes of egg-white and PAAm gels: the peak of the elastic loss tangent appeared before \( t'_{g} \) and thereafter, around \( t'_{g} \) the elastic stiffness increased up to \( \sim 10^3 \) times the initial value[7,8].

In the DSC measurements, we have reported that the transition behavior of NIPA/SA gel is complicated in low water contents. Water content \( w_c \) means the ratio of weight of water to that of network. The range of \( w_c \) is from 0.01 to 1.7 [9,10]. In the heating process, the DSC thermogram of NIPA gel shows the heat capacity gap (I) by glass transition in the range from \( w_c = 0.01 \) to 1.5, an endothermic peak (II) around 34°C at \( w_c = 0.35 \) and above, an endothermic peak (III) by melting of water above \( w_c = 0.85 \), and an exothermic peak (IV) appearing in the lower temperature side of the peak III at the range from \( w_c = 1.0 \) to 1.5. The peak II is related to the volume phase transition. It is well known that the NIPA gel in very high water content undergoes a continuous volume change around 34°C [11].

We carried out the dynamic viscoelastic measurements, in order to elucidate the mechanical behavior of NIPA gels in low water content below freezing point [12]. The transition point observed by the dynamic viscoelastic measurements corresponds well to the results of DSC measurements. It is also found that the real component of viscoelastic stiffness \( (E') \) dipped steeply around glass transition temperature. At the same time, a sharp peak of the elastic loss tangent \( (\tan \delta) \) was observed there. The \( E' \) showed the broad peak at temperatures between glass transition temperature and freezing point of water.
In a previous study, sol-gel transition of egg-white in low water content and the result of the thermal behavior of the gels was reported (Fig. 1) [13]. The results were compared with those of synthesized gel such as NIPA to examine universality of the appearance of complicated thermal behavior in low water content. In a sol-gel transition process, three endothermic peaks were observed. The peak temperatures are increased as the water content $w_c$ is reduced ($w_c < 1$). The thermal behavior of egg-white gel showed complicated behavior similar to the NIPA gel in low water content.

It is interesting to note that the water content, especially in low water content region, plays an important role to control the stiffness of the gel. This fact opens to the application of the food science and technology, if examined for the bio-related gels such as food materials.

In this paper, sol-gel transition of albumin in low water content and the result of the thermal behavior of the gels are also reported. The egg-white has various components and fifty-four percent of the main component are albumin. The results are compared with those of egg-white gel. The differences and similarities are clarified between these gels.

2. EXPERIMENTALS
2.1 Sample preparation
Albumin sol was prepared by dissolving albumin of chicken egg (Wako Pure Chem. Indus., Ltd) in distilled water. The water content of the samples were varied by dehydration under atmosphere. In order to homogenize the water content distribution in the sample, it was sealed in a closed vessel and left for a day. The water contents, $w_c$, is defined by:

$$w_c = \frac{w_{\text{water}}}{w_{\text{dried gel}}}$$

where $w_{\text{water}}$ and $w_{\text{dried gel}}$ represent the weights of water in the gel and the gel network, respectively.

The dry weight of the sample was estimated by heating it up to 125°C. The $w_c$ was varied from 0.19 to 3.34.

2.2 Measurements
DSC measurements were carried out using a SSC/5200 (Seiko Denshi Instr., Tokyo, Japan). The sealed type sample pans were used. All samples were
subjected to the heating-cooling-heating cycle. DSC curves were obtained in the temperature range from -80 to 110°C at a scanning rate of 3°C/min. The weight was measured on a microbalance (Mettler-Toledo Ltd., Model MT5) accurate to ±0.001mg.

3. RESULTS AND DISCUSSION

Figure 2 shows typical DSC heating thermograms of albumin sol with various water contents in the sol-gel transition process. In the sol-gel transition of albumin, peak intensity of low temperature side was strong in \( w_c = 0.67 - 3.24 \), and then in the \( w_c \) ranging from 0.27 to 0.54 peak intensity of high temperature side was strong. However, in the egg-white, peak intensity of the high temperature side was strong continually in a measured \( w_c \) range. Figure 3 shows the \( w_c \) dependence of the endothermic peak temperature (a, b, c, d, e) obtained from the DSC thermograms (Fig. 2). In a sol-gel transition process, four endothermic peaks were observed. The peak temperatures are increased as the water content \( w_c \) is reduced (\( w_c < 1 \)). The peak b (open square) were observed newly below \( w_c = 0.64 \) in low temperature side, whereas such peaks were not observed sol-gel transition in egg-white. The peak d overlap with peak e with decreasing water content around \( w_c = 0.6 \) as shown in fig. 3 (solid circle), and then these seem to be connected to one peak a. This seems to be due to a changing denaturing mechanism of the albumin greatly with very high concentration below \( w_c = 0.64 \). In the egg-white sol, three endothermic peaks were observed in the sol-gel transition process [13]. Here, the peak e of the albumin roughly corresponds to the endothermic peak of the high temperature side of the egg-white. Therefore, it is thought that the endothermic peak of the high temperature side of the egg-white attributes to the denaturation process of albumin. Furthermore, in the egg-white, the endothermic peak corresponding to peak b, c and d was not observed. It should be considered that other components in egg-white bind to the albumin molecules at a stage of peak e. It is found that the sol-gel transition of albumin developed in the single component in multistage.

Figure 4(a) shows typical DSC heating thermograms of albumin gel with various water content in the heating process. i, ii, iii endothermic peaks; iv, heat capacity gap. (b) The enlarged view of the DSC thermograms of \( w_c = 0.42 \) to 0.86. The broken line represents the heat capacity gap of the base line.

Fig. 4. (a) Typical DSC heating thermograms of albumin gel with various water content in the heating process. i, ii, iii endothermic peaks; iv, heat capacity gap. (b) The enlarged view of the DSC thermograms of \( w_c = 0.42 \) to 0.86. The broken line represents the heat capacity gap of the base line.

Fig. 5. The \( w_c \) dependence of the endothermic peaks (i, ii, iii) temperatures, the heat capacity gap (iv) temperature and faint peak (a, ▲, ▼) temperatures obtained from the DSC thermograms (Fig.4) in the heating process.
contents. Figure 4(b) shows the enlarged view of the DSC thermograms because peak intensity is weak with $w_c = 0.42 \text{ to } 0.86$. The $w_c$ dependence of the peak temperatures and the heat capacity gap temperature obtained from the DSC thermograms (Fig. 4) are depicted in Fig. 5. The temperature of heat capacity gap iv decreases rapidly with increasing water content up to $w_c = 0.6$, while it is constant (around $-64^\circ\text{C}$) above $w_c = 0.6$, and then disappears at $w_c = 0.9$. This gap is ascribable to the vitrification bound water and net work of albumin.

Figure 6(a) shows a plot of the enthalpy change versus water content calculated from the peak i and ii area in DSC thermograms in the albumin gel. The solid line is the theoretical line of the heat of fusion change assuming that all the water in the sample freezes around $0^\circ\text{C}$ into normal ice.

We have already reported the heat of fusion of water in egg-white gels as shown in figure 6(b)[13]. In this case, the free water disappears at $w_c = 0.4$, above $w_c = 0.4$, the amount of free water increases linearly up to $w_c = 0.9$ and then above $w_c = 0.9$, the heat of fusion increases parallel to solid line. The thermal behavior of albumin gel showed complicated behavior similar to the egg-white gel. It might be interesting to carry out further study to clarify the differences and similarities between these bio-related and synthesized gels.

References

Fig. 6(a). Plot of the enthalpy change versus water content calculated from the peak i and ii area in DSC thermograms in the albumin gel. The solid line is the theoretical line of the heat of fusion change when it is assumed that all the water in the sample freezes around $0^\circ\text{C}$ into normal ice.

Fig. 6(b). Plot of the enthalpy change versus water content calculated from the peak ($\Diamond$) area in DSC thermograms in the egg-white gel. The solid line is the theoretical line of the heat of fusion change when it is assumed that all the water in the sample freezes around $0^\circ\text{C}$ into normal ice. [13].

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