

## Property Change in Some Synthesized Gels by Dehydration

Kazuhiro Hara, Masaaki Sugiyama\*, Atsushi Nakamura\*\*<sup>1</sup>,  
Nobuyasu Hiramatsu\*\*<sup>2</sup> and Atsushi Suzuki\*\*\*

Fac. Eng., Kyushu Univ., Hakozaki, Higashi-ku, Fukuoka 812-8581

Fax: 81-92-633-6958, e-mail: haratap@mbox.nc.kyushu-u.ac.jp

\*Fac. Sci., Kyushu Univ., Hakozaki, Higashi-ku, Fukuoka 812-8581

Fax: 81-92-642-2553, e-mail: sugi8scp@mbox.nc.kyushu-u.ac.jp

\*\*Fac. Sci., Fukuoka Univ., Nanakuma, Jonan-ku, Fukuoka 814-0180

<sup>1</sup>Fax: 81-92-865-6030, e-mail: nakamura@ssat.fukuoka-u.ac.jp

<sup>2</sup>Fax: 81-92-865-6030, e-mail: hiramats@ssat.fukuoka-u.ac.jp

\*\*\*Fac. Eng., Yokohama Nat. Univ., Tokiwadai, Hodogaya-ku, Yokohama 240-8501

Fax: 81-45-339-3846, e-mail: suzuki@post.me.ynu.ac.jp

Gels turn into glasslike substances by being left in a dry atmosphere for a while. During the dehydration process, weight decreases through two stages corresponding to loss of the free water and bound water. There also occur anomalies in other properties (elastic stiffness, temperature etc.) during the dehydration process. Their results indicate that some transition takes place around  $t_g'$ . We also found emergence of a low frequency mode around  $t_g'$  in the dehydration process of PAAm gel, which well corresponds to Raman spectral features of the glass (amorphous) material. In addition to the measurements during the dehydration process, we also measured the evolution of Raman spectrum of the dehydrated PAAm gel with increasing temperature, and found that the intensity of the low-lying mode decreased remarkably. However, the broad band was still observed far above the transition temperature identified by thermal and elastic stiffness measurements. Such feature can come from inhomogeneity in the dehydrated gel.

Key words: gel, dehydration, glass, inhomogeneity, Raman

### 1. INTRODUCTION

Roughly speaking, gel is a two-component system with polymer network and solvent; one of the most attracted phenomena due to the interaction between these two constituents can be the volume phase transition<sup>1</sup>. There can be also other interesting phenomena due to their interaction. Among them, we have been much interested in the property evolution during dehydration process, which was firstly reported on heat-treated egg white gel (HTEWG) by Takushi *et al.*<sup>2</sup> By dehydration, opaque HTEWG turns into a transparent substance like glasses or plastics. From then, some investigations on evolution of properties have been performed during dehydration process of the egg white gel and some synthesized gels.

Let us describe the property change during the dehydration process of HTEWG more in detail. According to the above-mentioned report on the dehydration process of HTEWG<sup>2</sup>, the logarithm of

weight can be fitted with two lines; the slope is steep in the early stage and gentle in the late stage. Hereafter, we will refer the characteristic time (where the time dependence alters) as  $t_g'$ . It is said that the weight decrease in the early period is mainly due to the loss of free water, while, after  $t_g'$ , that of the bound water<sup>2</sup>. As can be easily understood, the property evolution during the dehydration is much affected with the surface tension of the solvent and/or the network strength<sup>3,4</sup>.

As well as the weight, elastic properties also show anomalies during the dehydration process. Koshoubu *et al.*<sup>5</sup> measured the elastic stiffness during the dehydration process of HTEWG. They found that the elastic amplitude increased up to  $10^3$  times the initial value at  $t_g'$ , and that the elastic loss tangent ( $\tan \delta$ ) shows a peak in the vicinity of  $t_g'$ ; these features resembled the temperature dependence (with decreasing temperature) of the elastic stiffness in the glass transition of noncrystalline polymers. Therefore, the

comparison between the dehydrated HTEWG and usual glasses became much informative. The most fundamental question was whether the glass transition could occur in the dehydrated HTEWG. In order to make clear that question, Kanaya *et al.* carried out the differential thermal analysis (DTA) measurements of the dehydrated HTEWG<sup>6</sup>. They found that an endothermic peak shifted to the higher temperature direction and the intensity became more intense with increasing the heating rate. From these characteristic features which are familiar in the glass transition<sup>7</sup>, it was concluded that the dehydrated HTEWG could be regarded as a glass.

Though interesting characteristics of the dehydrated gel were revealed by the studies of the HTEWG, as mentioned above, physical interpretations of observations are often very difficult because the egg white consists of various kinds of protein and other elements. Therefore, in the present study, we adopted the polyacrylamide (PAAm) gel as a model of the egg white gel, which is much simpler synthesized chemical gel, and observed property evolutions during the dehydration process, and those of the dehydrated gel during temperature increasing process.

## 2. EXPERIMENTAL AND RESULTS

### 2.1 Basic properties

We prepared the PAAm gel by heating the precursor solution (2g of acrylamide, 106mg of NN'-methylenebisacrylamide, 40mg of ammonium persulfate and 40mL of water) at 50°C for 2h. Then, the obtained gel was soaked in distilled water to wash out unreacted ingredients.

Roughly speaking, during the dehydration process, the weight and volume decreased up to around 5% and 7% of the initial values, respectively. Logarithms of them could be approximately fit by two straight lines, which were similar to their evolution during the dehydration process of HTEWG. In contrast, the density was almost constant, namely, the gel shrank in the same manner with the weight. These results indicated that the gel network was not strong enough to maintain their shape during the dehydration.

### 2.2 Anomalies in Elastic and Thermal Properties during Dehydration Process

A rectangular parallelepiped (5.4mm × 6.1 mm

× 38.1mm in size, 1267.1mg in weight) shaped sample was prepared for observing elastic anomaly during dehydration process with a vibrating (10Hz) elasticity measurement system. (In the measurement, temperature and humidity were within a ranges of 14.4 to 15.9°C and of 49 to 53%, respectively.) In the early stage, the elastic stiffness amplitude increased gradually. Then, around  $t_g'$ , the amplitude became 1000 times as large as the initial value and its increasing rate slowed down being saturated around  $10^8\text{N/m}^2$ . As for the elastic loss tangent, it showed a peak around  $t_g'$ . These features were similar to those of HTEWG during dehydration process. These resemblance revealed in the elastic anomaly indicated the similar transition mechanism. Besides, the value of the final elastic stiffness after dehydration was almost equal to that of HTEWG, which was much smaller (100 times) than usual polymers. This difference can come from the indirect contact of the polymer network through the layer of the bound water in the dehydrated gel.

Anomaly during the dehydration process was also observed in the evolution of the temperature. Two identical disk-shaped PAAm gel samples were prepared; one was used for the weight and volume measurement, and the other, for the temperature measurement. The temperature evolution of the PAAm gel disk was measured by using a differential thermal analysis apparatus. One of two connected thermocouples, of which the polarizations were set oppositely, was put into the disk-shaped gel and the other, left in the atmosphere ( $19.0 \pm 0.3^\circ\text{C}$ ;  $70 \pm 5\%$  in humidity). In the early stage, the temperature of the wet gel was lower than the atmospheric temperature due to the heat loss by water evaporation. Then, the temperature showed a step-like increase from  $-7.8^\circ\text{C}$  below room temperature to  $-0.12^\circ\text{C}$  around  $t_g'$ . After then, it remained almost constant until the end of the measurement; when the free water had been used up, the heat inflow from environmental atmosphere could exceed the small evaporation heat loss due to the bound water evaporation, therefore, the temperature of the gel could approach room temperature around  $t_g'$ .

### 2.4 Raman Scattering Measurement

#### 2.4.1 Experimental Configuration

As described in the previous sections, we observed several anomalies around  $t_g'$ . In addition to

those observations, we conducted the Raman scattering measurement during the dehydration process of wet PAAm gel and temperature increasing process of the dehydrated gel in order to investigate the dynamical features.

Experimental configurations in the Raman scattering measurements were as follows. A light source of 5145 Å from a vertically polarized Ar<sup>+</sup> ion laser and the right angle scattering geometry were adopted; the vertically-polarized scattered light from the specimen was analyzed by a triple monochromator. The resolution of the monochromator was 0.5cm<sup>-1</sup> in the observations of a low-frequency region from -550cm<sup>-1</sup> to 550cm<sup>-1</sup> and 20cm<sup>-1</sup> in those in the higher frequency region.

#### 2.4.2 Evolution of Raman Scattering Spectrum during Dehydration Process

In the Raman scattering measurement during the dehydration process, two identical rectangular parallelepiped specimens were cut out from the purified gel block mentioned above. One was used in the Raman scattering measurement, and the other, in the simultaneously-performed weight measurement, which were conducted under almost the same conditions (temperature range from 22 to 24 °C and in a humidity range from 45 to 55%). By close examination, evolution of the logarithmic weight could be fit by three straight lines: the first stage from 0 to 65000s ( $t_c'$ ), the second stage from  $t_c'$  to 93000s ( $t_g'$ ) and last stage from  $t_g'$  to the end of the measurement.

In beginning of the first stage, only a diffusive central mode was observed in the low frequency region. Then after  $t_c'$ , width of the diffusive central mode became narrow and a shoulder-like profile appeared on the skirt of the diffusive central mode. With successive narrowing of the central mode, the shoulder became a broad peak after  $t_g'$ ; the central mode could not be distinguished from the elastically scattered spectrum at last.

As for the high-frequency Raman spectrum, a remarkable decrease in the peak intensity of the mode located around 3200cm<sup>-1</sup> was observed, which is known to correspond to the O-H stretching vibration of pure water [8]. With the continuous decrease in the intensity, the mode disappeared after around  $t_g'$ . In the previous experiment, as mentioned above, a step-like increase in the tem-

perature was observed around  $t_g'$ , which is due to the loss of the free water in the gel. Because the free water molecules in the gel are almost in the same conditions with the pure water [8, 9], the extinction of the 3200cm<sup>-1</sup> mode after  $t_g'$  showed directly the complete exhaustion of the free water in the gel.

In the field of the sol-gel science (mainly on the inorganic gels), drying of the wet gel [10] and the heat induced gel-to-glass transition of the dehydrated gel [11] have been extensively investigated. The above-mentioned gel-to-glass transition in the sol-gel science is a heat-induced transition in which the porous dried gel changes into glass by collapse of the pores. In a sense, the features in the gel-to-glass transition resembles our *gel-to-glasslike* transition during the dehydration process, though the dehydrated materials of these studies are porous and different from our dense glasslike substance. There have been many reports on the low-frequency Raman measurements in the studies on gel-to-glass transition [12-16]; among them, they reported the emergence of a low-lying Raman band in the heat-induced transition. The low-lying mode is called *boson peak*, which is commonly observed in glasses or amorphous materials, although its nature remains a matter of controversy [17].

Some of their results can be used to explain the Raman spectral anomalies during the dehydration process, namely, the low-lying Raman band appearing during the dehydration process of PAAm gel can be the boson peak. However, we were also aware of the difference in the value of the low-lying mode frequency between our dehydrated gel and usual glasses. In our glasslike dehydrated PAAm gel, the mode lay around 80cm<sup>-1</sup>, while in the glass substance, usually around 30cm<sup>-1</sup> [12, 13].

#### 2.4.3 DSC, Elastic stiffness and Raman Scattering Measurement with Increasing Temperature

From the experimental results described in the previous sections, to measure the temperature dependent properties of the dehydrated PAAm gel and to compare the results with the usual glasses seemed important and interesting. Therefore, we carried out the thermal, elastic stiffness and the Raman scattering measurements of the dehydrated PAAm gel with increasing temperature.

The thermal property with increasing temperature was measured with a differential scanning calorimeter (DSC) analysis system. The temperature increas-

ing rate during the measurement was 10°C/min. In the DSC curve, an anomaly was clearly observed around 60°C.

In the elasticity stiffness measurement, a forced vibration (frequency, 1 Hz) apparatus was utilized in the three-point bending mode; the measurement was carried out with increasing temperature at a rate of 8 °C/min. The real and imaginary parts of the elastic stiffness simultaneously showed anomalies (remarkable decrease and a broad peak, respectively) around 60°C.

As for the Raman scattering measurement, at room temperature, a low-lying peak with a maximum around 80cm<sup>-1</sup> was clearly observed as mentioned in the previous section. The intensity of the peak became lower with increasing temperature, however, the peak could be still distinguished far above the temperature where the thermal anomaly was observed (even at 90°C).

The features observed in the DSC and elastic stiffness measurements indicate that the glass transition occurred in the macroscopic scale around 60°C. As is well-known, the glass transition temperature will be lowered with decreasing the heating rate. Therefore, the glass transition temperature in the Raman scattering measurement was considered to be below 60°C, because the Raman scattering measurement took more time than the DSC and elastic stiffness measurements. Therefore, the Raman scattering spectrum at 90°C was measured far above the glass transition temperature. Considering these circumstances, the dehydrated PAAm gel was considered to be composed of weakly joined hard amorphous clusters of which the frozen structure can be maintained even far above the macroscopic glass transition temperature.

#### ACKNOWLEDGMENT

This work was partly supported by Grant-in-Aid for Scientific Research of The Ministry of Education, Science and Culture.

#### REFERENCES

1. T. Tanaka, *Sci. Am.* 244, 124 (1981) .
2. E. Takushi, L. Asato and T. Nakada, *Nature* 345, 298 (1990).
3. H. Kanaya, K. Ishida, K. Hara, H. Okabe, S. Taki, K. Matsushige and E. Takushi, *Jpn. J.*

- Appl. Phys.* 31, 3754 (1992).
4. H. Kanaya, K. Hara, E. Takushi and K. Matsushige, *Jpn. J. Appl. Phys.* 32, 2905(1993).
5. N. Koshoubu, H. Kanaya, K. Hara, S. Taki, E. Takushi and K. Matsushige, *Jpn. J. Appl. Phys.* 32, 4038(1993).
6. H. Kanaya, T. Nishida, M. Ohara, K. Hara, K. Matsushige, E. Takushi and Y. Matsumoto, *Jpn. J. Appl. Phys.* 33, 226(1994).
7. T. Nishida, T. Ichii and Y. Takashima, *J. Mater. Chem.* 2, 733(1992).
8. T. Terada, Y. Maeda and H. Kitano, *J. Phys. Chem.* 97, 3619(1993).
9. K. Ogino, Y. Osada, T. Fushimi and A. Yamauchi, *Geru --Sofutomateriaru no Kiso to Oyo- (Sangyo Tosho, Tokyo, 1991) p.14 [in Japanese].*
10. G. W. Scherer, *J. Non-Cryst. Solids* 100, 77(1988).
11. P. F. James, *J. Non-Cryst. Solids* 100, 93(1988).
12. G. Mariotto, M. Montagna, G. Viliant, R. Camprostrini and G. Carturan, *J. Non-Cryst. Solids* 106, 384(1988).
13. J. L. Rousset, E. Duval, A. Boukenter, B. Champagnon, A. Monteil, J. Serughetti and J. Dumas, *J. Non-Cryst. Solids* 107, 27(1988).
14. J. Dumas, J. Serughetti, J. L. Rousset, A. Boukenter, B. Champagnon, E. Duval and J. F. Quinson, *J. Non-Cryst. Solids* 121, 128(1990).
15. K. Dahmouche, C. Bovier, A. Boukenter, J. Dumas, E. Duval, C. Mai and J. Serughetti, *J. Phys. IV* 2, Colloq. C2-127(1992).
16. A. Chmel, A. Krivda, E. Mazurina, V. Shashkin, and V. Zhizhenkov, *J. Am. Ceram. Soc.* 76, 1563(1993).
17. R. A. Ramos, *Phys. Rev. B* 49, 702(1994).

(Received December 19, 1998; accepted April 14, 1999)