

Temperature Dependence of Low-Frequency Relaxation of Dehydrated Gel

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Dehydrated (heat-treated egg white and polyacrylamide) gels show elastic anomalies around a characteristic temperature: a peak in the loss tangent (or imaginary part) and thousands-time change in amplitude (or real part) of the complex elastic stiffness. Their frequency dependence also revealed characteristic features on the relaxation process which characterizes the glass transition: decrement of the relaxation period in the temperature elevating process, indicating the dehydrated gel to be a normal polymer glass.

Key words: dehydrated, gel, elastic, frequency, glass transition

1. INTRODUCTION

Because of made of the two components, polymer network and solvent, the gel shows intermediate property between liquid and solid due to the ingredients' interaction. Besides, with change in their interaction, it shows unique properties such as the well-known volume phase transition [1].

The authors have been investigated the property change during the dehydration process of the hydrogel. The dehydration of the hydrogel is interesting because the drastic property change can be expected; the gel is composed of the water (solvent) and the polymer network, as mentioned above, and the dehydration means exhaustion of one of the two indispensable components, therefore.

On the property change of the hydrogel during the dehydration process, the first scientific report was made by Takushi *et al.* [2]: two characteristic stages were revealed by the different linear time dependences of the logarithmic weight decrement, which altered at a certain time (t_g'), during the dehydration process of the heat-treated egg white gel. This feature indicated that the ma-

ior part of the evaporating solvent changed from the free water to the bound water around t_g' [2-4], when several quantities showed anomalies due to the interaction change. The first demonstrations of the ingredients' interaction change were made in the property changes during the dehydration process of differently-treated egg white gels: the marked volume decrement in the heat-treated gel against almost constant one in the pressurized gel [5], and remarkable variation in the shrinking behaviors with exchanging the solvent [6].

Such a feature was also observed in the elastic property: increment in the amplitude of complex elastic stiffness up to thousands times the initial value and a clear peak in the elastic loss-tangent ($\tan \delta$) around t_g' [3, 7], which looked like the elastic behaviors in the glass transition of noncrystalline polymers [8]. From these behaviors, we have been considering the mechanism of the elastic anomalies as follows: During the dehydration process, the water diminution can shorten the distance between the network polymers with the capillary force of the remnant water in the hydrogel, then, the increasing interaction between the neighboring network chains will ham-

per the thermal motion of the network polymer. In this procedure, the freezing of thermal motion can occur like the glass transition of the noncrystalline polymer. As to the structure, no sharp peak in the dehydrated egg white gel was already confirmed by X-ray diffraction experiment, which means that there is no crystalline region [2,5,6].

The authors have been also interested in comparison of the products, namely, the dehydrated gel and noncrystalline polymer glass because of the above-mentioned elastic property evolution analogy in the formation processes. Therefore, a differential thermal analysis (DTA) was carried out during the temperature elevating process for the examination of the thermal property of the dehydrated heat-treated egg white gel; a clear endothermic peak was observed, of which the intensity and temperature became higher with the temperature elevation rate [9]. It was concluded that the dehydrated gel could be regarded as a kind of glass because such a behavior has been frequently observed in the glass transition of noncrystalline polymers [10].

It is well-known that the noncrystalline structural feature can be examined by nonexistence of acute peaks in the X-ray diffraction profile. In addition to this structural characterizations, there are several analyses which characterize the vitreous feature of the noncrystalline material. Among them, the authors adopted the Raman scattering spectrum method and performed the observations during the dehydration process of PAAm gel, simultaneously measuring evolution of the weight [4]. Because the peak intensity of the 3200 cm^{-1} mode reflects the abundance of the water in the hydrogel, we could examine the decrement of the water in the PAAm gel during the dehydration process [11]: the peak intensity became smaller, and after t_g' , the peak could not be distinguished. This behavior coincided with the evolution anomaly in the weight which indicated free water dissipation at that time [3]. In addition to the disappearance of the high frequency Raman mode, a change in the low frequency spectrum attracted the authors' interest. In the early stage of the dehydration process, only a diffusive skirt was observed around the elastic scattering peak in the low frequency Raman spectrum. The width of the diffusive skirt became narrower with progress of the dehydration, and around t_g' , there appeared broad sideband

peaks in the low frequency region. Such a low-lying Raman peak was also observed in the dehydrated heat treated egg white gel around almost the same frequency region [13]. Because the existence of a low-energy excitation named *Boson peak* has been well-known in many amorphous materials, the observed low-lying band seemed to be the Boson peak. However, in spite of the aforementioned qualitative similarity, a quantitative difference between the dehydrated gel and polymer glass has been also noticed on the peak frequency of the low-lying mode: the low-lying mode in the dehydrated gels were around 80 cm^{-1} [4,13], while the Boson peak frequency of many polymer glasses is around 30 cm^{-1} [14].

In order to find the reason for these features, the temperature dependence of the sideband in the dehydrated PAAm gel was measured with increasing temperature, performing the dynamic elasticity (at 1Hz) measurement and differential scanning calorimetry (DSC) measurement simultaneously [16,17]. Almost the same elastic behavior was observed as shown in Fig.1 [18].

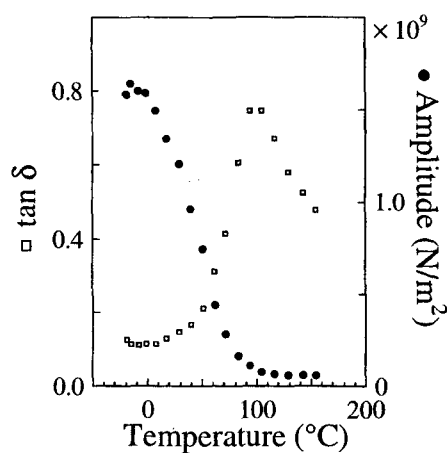


Fig.1 Temperature dependence of the amplitude and loss tangent of complex elastic stiffness [18].

Though anomalies were coincidentally observed around 60°C (T_g) in both the DSC and elasticity measurements, which has been observed in many polymer glasses, an attention-getting feature was also revealed in the temperature dependence of the low-lying Raman mode, which could be observed even far above T_g determined by the thermal and elastic measurements. This features seemed to come from a fundamental property of the dehydrated gels. Then, in order to work through these superficial inconsistency,

an inhomogeneous structure composed of the weak-linked high- T_g clusters has been assumed [16,17].

However, there have been no direct basis for such an assumption, therefore, the solution of this inconsistency has seemed important subject for understanding the properties of the dehydrated gels. Therefore, in the present study, the reexamination of the evolution of the elastic property was performed by its temperature and frequency dependence.

2. EXPERIMENTALS AND RESULTS

The pre-gel solution was a mixture of acrylamide (2g), NN'methylenbisacrylamide (106mg), ammonium persulfate (40mg) and water (40ml). By heating this solution at 323K for 1hour, a polyacrylamide gel block was obtained. The block was washed by immersing in distilled water for a week. After this purification, the gel block was dried in a refrigerator (temperature 5°C, humidity 60%) for a month. The water content [3] of the dehydrated specimen was around 0.17. The dried gel was transparent and hard just like plastics. Then, the dehydrated gel block was cut into sheet-shaped ($33.6 \times 5.78 \times 0.63 \text{mm}^3$) samples. In order to prevent the water content change in the measurement, the samples were covered with very thin silicone grease layer.

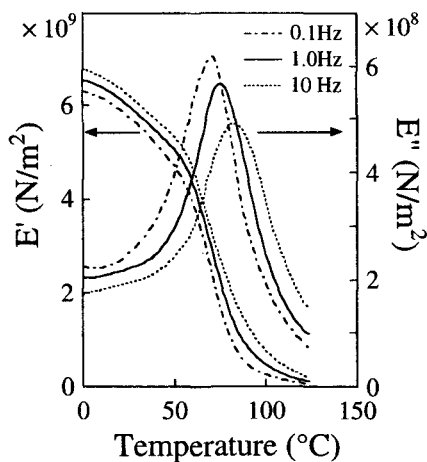


Fig.2 Temperature dependence of the real and imaginary part of complex elastic stiffness at several frequency.

In the elasticity measurement, a vibrometer (Seiko Denshi Model DMS110) was utilized in a

three-point bending mode. In order to examine both of the frequency dispersion and sample variation, two samples were measured in the overlapped frequency ranges, R1 (from 0.1 to 10Hz) and R2 (from 1 to 50Hz). The temperature increasing rate was 2deg/min.

Figure 2 shows the temperature dependence of the elastic stiffness at several frequencies. The real part (E') showed remarkable decrease around at some temperature (T_g). As to the imaginary part (E''), a clear peak was observed around T_g . The positions of these profiles shifted toward the higher temperature with frequency. These behaviors corresponded to those in the previous fixed frequency measurements.

3. DISCUSSIONS

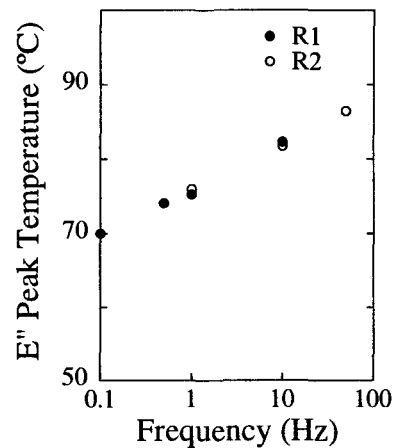


Fig.3 The relation between the applied frequency and peak temperature of the imaginary part of complex elastic stiffness.

The elastic stiffness at 1Hz in the present study showed almost the same temperature dependence with that in the previous investigation [17]. From the frequency dependence of the elastic stiffness evolution revealed in the present investigations, the more detailed characterization of the glass transition of dehydrated PAAM gel can be done as follows.

As mentioned above, E'' showed a peak at some temperature; the peak temperature of E'' at several frequencies is depicted in Fig.3. As can be easily seen from the figure, the data almost coincided in the overlapped frequency range of R1 and R2, therefore for further examinations, their mean value is used.

The examination of the temperature dependence of the relaxation period (τ) seems very important because the glass transition is a freezing process of the

elastic relaxation.

In order to estimate the evolution of τ , the relation, $\tau = 1 / \omega$ (which holds at the peak temperature in the simple relaxation process [19,20]) was utilized in the present study. In the equation, ω is the applied angular frequency. The temperature dependence of τ is shown in Fig.4; τ decreased so much with increasing temperature, which means that the specimen behaves like a fluid. The activation energy of the relaxation process could be estimated from Arrhenius' plot [20] around 90 kcal/mol, which is within the range of many normal polymer glasses.

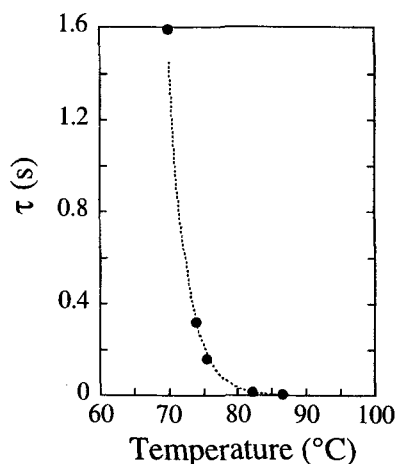


Fig.4 Temperature dependence of the relaxation time.

In the present investigation, it has been confirmed that the dehydrated PAAm gel is a normal polymer glass from the elastic point of view and that above-mentioned inconsistency does not come from the binding force governs the macroscopic transition. At least, the result in the present investigation does not conflict with the inhomogeneous structure model. Therefore, the next thing to be done is the more detailed examination of the dynamical properties, for which the inelastic neutron scattering will be favorable because it can directly probe the dynamics.

ACKNOWLEDGMENTS

This work was partly supported by a Grand-in-Aid from the Ministry of Education, Science, Sports and Culture.

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(Received December 17, 1999; Accepted March 31, 2000)