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Characterizations of Dynamics in Dehydrated Gels by Low-Frequency Raman Scattering

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Raman scattering investigation of dehydrated PAAm/SA gel with different amount of *NN'*-methylen-bisacrylamide (cross-linker) was carried out in order to elucidate effect of an inhomogeneity on the low-frequency Raman scattering spectrum. In a low cross-linker concentration region, a low-frequency excitation which is thought to be related to the network cross-link dominates in the Raman spectrum, while, in the higher concentration region where the wet gel becomes turbid, a peak located in the lower frequency becomes prominent. The feature indicates a considerable structural change in a nano-meter scale.

Key words: gel, inhomogeneity, low frequency excitation, Raman scattering, dehydration

1. INTRODUCTION

1.1 *Dehydration of Gels*

Gels are composed of polymer network and solvent, which show interesting properties by the interaction between the constituents. Among the characteristic phenomena, the volume phase transition [1] is the most famous phenomenon. However, the authors believe that there are also interesting features other than the volume phase transition, and have been interested in the property evolution when the solvent of the hydrogel is taken away, namely, during the dehydration process, which is interesting because the solvent (water) is one of the two indispensable components making up the gel as mentioned above, therefore, the drastic property change can be expected by the dehydration. Actually, features during the dehydration process of gel are much influenced by some interactions between network polymer and solvent. By dehydration, the gel converts into a glass-like substance and, in the dehydration process, several properties show distinct changes simultaneously at a certain time. The first scientific report on this phenomenon was done by Takushi *et al.* on heat-treated egg-white gel [2]. By dehydration, an opaque egg white gel turned into a transparent substance like a glass; we call the transition "gel-to-glasslike transition." After the first report of the gel-to-glasslike transition by Takushi *et al.*, investigations on the property evolution of the dehydrating gels have been extensively carried out.

Let us move to more concrete topics. In the first study of the glass-to glasslike transition by Takushi *et al.* [2], it was found that the logarithm of weight shows a proportional decrease to the measurement time and that its slope alters at a certain time (t_g') during the dehydration process of the heat-treated egg white gel. They concluded that the steep linear decrease in the early period is due to the free-water loss, while that more gentle one after t_g' results from loss of the bound water. Such features are also influenced by the property of the constituents, namely the network and solvent (water). Kanaya *et al.* carried out the time-resolved simultaneous weight-and-volume measurements during the dehydration process of the heat-treated (at 100°C for 12min, abbreviated as HTEWG hereafter) and the pressure-treated egg white gel (at 500MPa for 60min, abbreviated as PTEWG hereafter) [3]. In the experiment, it was found that, while their weights show a similar decrease, their volumes show considerably different features during the dehydration process: the volume of HTEWG decreases as its weight does, while that of PTEWG remains at its initial value. This different can come from a competing situation between the capillary force of internal free water and the network polymer-chain elasticity which differs with the treatment through different degrees of denaturation [4]. In order to elucidate the effect of the capillary force, Kanaya *et al.* also observed the dehydration process of the hydrogels of which the solvents are substituted with several fluids of different surface tensions [5]. In the experiments, the HTEWG's solvent-substituted with ethanol and acetone become turbid porous substances. Besides, they do not show the clear transition point in the time dependence of the logarithm of weight during the dehydration process. In this case, the capillary force of the residual solvent is much less than that of the water, which shows how the interaction between the network and residual solvent affects the property in dehydration process. The interaction between the network and the internal solvent also influences the elastic property of dehydrating gels. Koshoubu *et al.*[6] measured the complex elastic stiffness of HTEWG during the dehydration process. With progress of dehydration, around t_g', modulus of complex elastic stiffness becomes several hundred times as large as that in fully wet state, and, just before then, elastic tanδ shows a peak. These behaviors are similar to elastic evolution in the glass transition of non-crystalline polymers which appears by changing temperature. They explained the similarity as follows. The free water is thought to be able to move relatively freely through compartments composed of the gel network, therefore, it acts as a lubricant which decreases interactions between network polymers. In this sense, it can be said that free water will keep the softness of the gel. In the dehydration process, by the capillary force of the remnant solvent, loss of free water shorten the distance between the network polymer and the crowded arrangement increases their interaction and suppresses their micro-Brownian fluctuation. Such a situation is analogous to the micro-Brownian motion freezing with decreasing temperature in the case of the glass transition of non-crystalline polymers. Therefore, the similar elastic anomaly will occur in both the dehydration process of HTEWG and the glass transition. From their elastic measurement, the important role of the internal free water to maintain the network polymer-chain fluctuation was demonstrated. In these circumstances, property comparison between dehydrated HTEWG and non-crystalline polymers was thought to be important by abovementioned their similarity and the most attractive theme was whether the dehydrated HTEWG would show a glass transition with increasing temperature. Kanaya *et al.* demonstrated the occurrence of the glass transition in the dehydrated HTEWG by DTA measurements with elevating temperature: they found an endothermic peak which shows characteristic behavior widely observed in the glass transition [8] and concluded that the dehydrated egg white gel could be regarded as a glass [7]. Their conclusion can support the formation mechanism similarity between the dehydrated HTEWG and the common glass mentioned above.

Though characteristic aspects of the gel-to-glasslike transition became somewhat clear by above-mentioned studies, the variety of ingredients in the egg-white often makes physical interpretation of the experimental results difficult. Besides, a more important thing is that the gel-to-glasslike transition seemed to occur generally in many gels [9]. In this sense, Masuike and Hara adopted a polyacrylamide (PAAm) as a specimen, which is one of the most popular chemical gel with the simpler ingredients compared with the egg white gel, and measured simultaneously evolution of weight, volume and temperature difference between the gel and atmosphere (ΔT) during the dehydration process [10]. By dehydration, the PAAm gel was found to also turns into a brittle and transparent substance. In dehydration process, both the weight and volume evolute in the same manner of HTEWG. From these features, the network elasticity of the PAAm gel was found to be weaker than capillary force of the remnant internal free water, which can be applies to the case of HTEWG. In addition, around t_g', they observed a step-like change in ΔT from a negative value to 0. This feature can be due to the exhaustion of internal free water which is easy to evaporate [11].

1.2 *Raman Scattering Spectrum Change by Dehydration*

The occurrence of the gel-to-glasslike transition in PAAm gel was also demonstrated by these experimental results. From a viewpoint of easiness to perform various experiments for investigating property change during the dehydration process, PAAm gel is thought to be suitable as a specimen for that purpose because of the simplicity of the ingredient as mentioned above. In addition to the ingredient simplicity, there is another reason to adopt PAAm gel for investigating property change during dehydration process. Especially in the case of the Raman scattering experiments, because PAAm gel is transparent before and after the dehydration, the detailed investigations on the dynamical properties can be easily performed without a strong elastic component in the spectrum. In these circumstances, Hara *et al.* performed time-resolved measurements both of the Raman spectrum and weight during the dehydration process of the PAAm gel in order to characterize the dynamical aspects during the dehydration process [12]. They examined the Raman scattering spectrum both in the low (0~550cm^{-1}) and high (above 550cm^{-1}) frequency regions [12]. The amount of the free water was estimated from the intensity of a peak at 3200cm^{-1} of O-H stretching mode of the free water molecule [13,14]. With progress of the dehydration process, the 3200cm^{-1} mode becomes small, and, around t_g', the peak vanishes when the logarithm of weight shows a bend as mentioned above, namely, the complete exhaustion of the free water at t_g' could be confirmed [15]. There occurs drastic change was also observed in the low frequency region of the Raman spectrum as follows: A diffusive central skirt is observed in the early stage and, with the dehydration proceeds, the diffusive mode became narrower. Then after t_g', width of the central skirt becomes negligibly small and a doublet can be perceived at that time.

1.3 *Inhomogeneity Occurrence by Surplus Crosslinker*

Some of chemically cross-linked gels are known to become turbid above a certain cross-linker concentration due to network polymer inhomogeneity with a scale of light wavelength. The PAAm gel is also known to become opaque and, in the case of PAAm gel, cross-linker concentration where the turbidity occurs is reported to be around 7.5 wt% [16]. It is also informed that NIPA gel becomes turbid above the temperature where the volume phase transition occurs around 32°C. Hirokawa *et al.* observed inhomogeneous network structure by observing the turbid NIPA gel by a laser scanning confocal microscope [17]. However, the previous studies are focused on structural and elastic light scattering features and there have been almost no studies on other property changes by the occurrence of the network inhomogeneity, which are thought to considerably affect the low-lying mode in consideration of the origin of the low frequency mode expected from the discussions mentioned above.

In these circumstances, we have observed cross-linker concentration dependence of the low-frequency Raman spectrum of the dehydrated PAAm/SA gel in the present study. By the investigations, we have found a considerable change in the mode as described following sections.

2. EXPERIMENTALS AND RESULTS

The PAAm/SA gel was obtained by heating, for 24 hours at 60 °C, precursor aqueous-solutions (acrylamide 500 mM, sodium acrylate 200 mM and ammonium persulfate 0.05 wt%) with different amounts of *NN'*-methylenbisacrylamide (cross-linker) from 0.5 wt% to 4.5 wt%. Before heating, all the solutions were transparent, while after the heat-treatment, the specimens with the cross-linker concentration above 2.5 wt% became turbid. Then, the gelled lumps were cut into plate-shaped specimens with a dimension of 10 mm×10mm×3mm. Then the plates were dehydrated in a desiccator (25 °C in temperature and 30 % in humidity) for 6 days after soaked in pure water for 24 hours in order to remove unreacted ingredients. The water contents of the dehydrated gels were below 20 %.

Raman scattering experiment was performed by a triple monochromator (JASCO NRS-2000) installed at Research Reactor Institute in Kyoto University. A light source of 6328 Å from a He-Ne laser was utilized with output of 100 mW. In the measurements, a quasi-back scattering geometry was adopted in order to avoid strong elastic scattering from the surface of the specimen. The resolution was around 20.7 cm^{-1}.

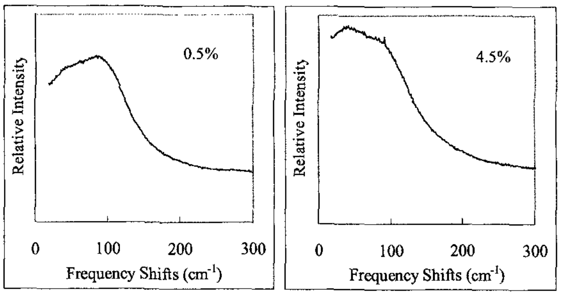

Fig.1 Low-frequency Raman spectra of dehydrated PAAm/SA gels with different cross linker concentrations. Numbers in the figures describe the cross-linker concentrations.

Figure 1 shows the low-frequency Raman scattering spectra of the dehydrated PAAm/SA gels with the cross-linker concentration below and above 2.5 wt% of the precursor solution. As can be easily seen from the figure, there are two peaks in the low-frequency Raman spectra: the peak with the higher frequency (around 80 cm^{-1}) is the one which were found in the previous investigation in the dehydrated PAAm gel and the peak with the lower frequency (around 30 cm^{-1}) is a newly recognized one.

3. DISCUSSIONS

Low-lying Raman spectral peaks are not frequently reported for non-crystalline materials; therefore, the investigations of them are important to understand the low energy excitation in these materials. Because of the similar spectral shape, the authors estimated that the 80 cm^{-1} peak might be a Boson peak, which is commonly observed in the low-lying Raman spectrum of the glass and amorphous material, when the authors found the low-lying peak in the Raman spectrum [12]. A similar doublet was also observed in the DHTEWG [18]. However, they have also noticed a difference between the feature of the low-lying peak of the dehydrated gel and that of common glass; the peak of the dehydrated gel is located around 80cm^{-1} [12,18], while that of common glass, usually around 30cm^{-1} [19,20].

Related to the spectral characteristics mentioned above, it may be needed to describe on a low-frequency Raman spectral difference between dehydrated egg white (DEW) and dehydrated HTEWG (DHTEWG) reported by Nakamura *et al.* [21]; a low-lying band is located around 80 cm^{-1} in DHTEWG similar to the dehydrated PAAm gel, while, in DEW, around 30 cm^{-1} and the spectral feature rather resembles the Boson peak. Roughly speaking, because structural characteristics of raw egg white and heat-treated egg white gel is aggregated globules and cross-linked coils mainly comes from denaturation of ovalbumin, respectively, the low-frequency mode around 30 cm^{-1} seems related to the aggregated globules without cross-link while that around 80 cm^{-1} can come from the cross-linked coils.

Because there was a necessity to clarify the origin of the 80 cm^{-1} mode in the Raman scattering spectrum of the dehydrated PAAm gel and to verify the existence of glass transition in it, Hara *et al.* carried out the thermal analyses with a differential scanning calorimetry (DSC) system and the observation of the temperature dependence of the low-lying Raman spectrum of the dehydrated PAAm gel [22]. In the thermal measurement with the DSC system, a clear bend point is perceived in an endothermic curve around 60°C. As to the low-lying mode in the Raman spectrum, the abovementioned peak located around 80cm^{-1} can be still distinguished even up to 90°C though the intensity becomes very low with elevating temperature as shown in Fig.2. Because the DSC-curve anomaly demonstrates occurrence of the glass transition around 60°C, the Raman scattering measurements with increasing temperature is thought to have performed up to far above the glass transition

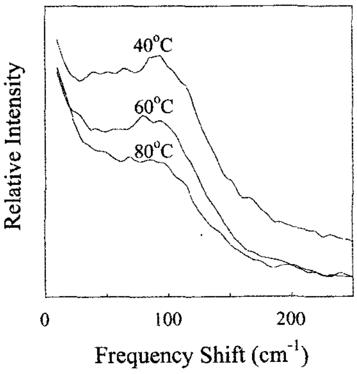

Fig.2 Temperature dependence of the low-frequency Raman spectrum of a dehydrated PAAm gel [22]. The glass transition temperature of the specimen is 60 °C.

temperature. In short, the 80cm^{-1} excitation in the dehydrated PAAm gel still exists far above the glass transition temperature, which seems very curious if the low-frequency peak is the so-called Boson peak observed in variety of amorphous materials. In order to explain both the experimental results which apparently seem contradictory to each other, they estimated an inhomogeneous structure composed of weakly joined clusters of which the internal structure is stable even far above 60°C. Taking the spectral features of DHEWG and DEW [21] into consideration, the rigid structure seems related to the cross-link in the gel, namely, the low-lying mode comes from a kind of inhomogeneity related to the cross-link.

As mentioned above, the higher frequency mode in the Raman spectrum is thought to come from the excitation related to the cross-linked polymer network. As for the lower frequency one, judging from the intensity increase when the gel becomes turbid, the mode should be closely related to an inhomogeneity with the scale of the light wave length. Besides, the frequency range where the lower mode exists is almost the same one of the so called Boson peak which is usually observed in the Raman spectrum of amorphous material composed of non-polymer materials and of the dehydrated raw egg white [18]. Therefore, the authors estimate the origin of the lower mode as follows: In the specimen with higher cross-linker concentration, degree of inhomogeneity is more increased as observed by increase in turbidity. The occurrence of the inhomogeneity indicates existence of the large network-polymer concentration fluctuation of which the structure can be large polymer clusters connected with thin network polymer. Because the elasticity of the thin string may be very weak, the large cluster in the estimated model can behave like the non-polymer particles in the inorganic amorphous materials and protein globules in the dehydrated raw egg white.

Though the more detailed investigations should be necessary in order to verify this estimation, the clear change in the low-frequency Raman spectrum by inhomogeneity has been found for the first time in the dehydrated gels, which should be very interesting and informative to study property change caused by the inhomogeneity.

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