

Mechanical Behavior of NIPA Gels in Low Water Content below Freezing Point

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In the DSC measurements, it was found that the transition behavior of *N*-isopropylacrylamide / sodium acrylate (NIPA/SA) gel in low water content is complicated, depending on the water content w_c . The thermogram shows the glass transition, an endothermic peak around 34°C and peaks related to the melting and recrystallization of water. In the present study, in order to elucidate the mechanical behavior of NIPA gels in low water content below freezing point, we carried out the dynamic viscoelastic measurements. 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 dipped steeply around glass transition temperature. At the same time, a sharp peak of the elastic loss tangent was observed there. The real component of viscoelastic stiffness showed the broad peak at temperatures between glass transition temperature and freezing point of water.

Key words: NIPA gel, low water content, glass transition, mechanical properties, differential scanning calorimetry

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 by 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 period 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 feature 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 composition simpler than that of egg-white gel, also becomes hard and transparent upon dehydration. The characteristic phenomenon was revealed by examining the time dependence of elastic stiffness during the dehydration process of egg-white gel and PAAm gel: 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 small angle X-ray scattering (SAXS) measurement, Sugiyama *et al.* [9] found a prominent peak in the SAXS profile probably

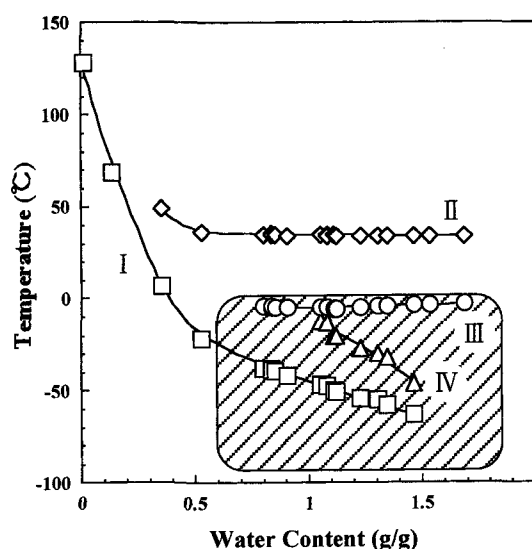


Figure 1. The w_c dependence of the heat capacity gap (I) temperature, the endothermic peaks(II , III) temperatures and exothermic peak(IV) temperature obtained from the DSC thermograms of NIPA(700mM) in the heating process.

attributed to the microphase separation during the dehydration of N-isopropylacrylamide(NIPA)/ sodium acrylate (SA) gel. The viscoelastic behavior of dried NIPA/SA gel was examined under the moisture and temperature controlled condition by us [10]. The results showed that the elastic modulus is gradually and then drastically decreases as the H_2O vapor pressure increases under constant temperature, and that the peak of loss tangent appeared around the moisture region of drastically decreasing modulus. It is well known that the NIPA gel in very high water content undergoes a continuous volume change [1]. In the differential scanning calorimetry (DSC) measurements, we have reported that the transition behavior of NIPA/SA gel in low water contents, (the ratio of weight of water to that of network, $w_c = 0.01 - 1.7$) is complicated, depending on the w_c [11,12]. In the heating process, the DSC thermogram of NIPA (700mM) 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 (figure 1).

In the present study, in order to elucidate the mechanical behavior of NIPA gels in low water content below freezing point in the hatching area in figure 1, we carried out the dynamic viscoelastic measurements. The assignments of the transitions observed were discussed.

2. EXPERIMENTALS

2.1 Sample preparation

Gels were prepared by a free radical copolymerization. N-isopropylacrylamide (700mM), the linear constituent, N,N'-methylenebisacrylamide

(BIS, 8.6mM), the tetra-functional cross-linking constituent, ammonium persulfate, the initiator (10mg), and sodium bisulfite (10mg), the accelerator, were dissolved in deionized, distilled, and nitrogen-saturated water at 20°C to a final volume of 50ml. The solution was then poured into glass tubes. After the gelation was completed, the gel was taken out from the glass tubes, and then immersed in water in order to wash away residual chemicals. We obtained dried NIPA gel by dehydrating the gel under atmosphere after cutting it in the shape of disk. The water content of the samples were varied by adding deionized and distilled water to the dehydrated NIPA gels using a micropipette. In order to homogenize the water content distribution in the sample, it was sealed in a closed vessel and left for several days. The dry weight of the sample was estimated by heating it to 125°C . The w_c was varied from 0.6 to 1.9.

2.2 Measurements

The dynamic viscoelastic measurements were carried out with a DVA-225(IT Keisoku Co. Ltd., Osaka, Japan) in the compression mode at a constant frequency of 10Hz and 0.15% strain. The sample size was about 2.0-2.5(t)mm and 5.5-5.2(ϕ)mm. The dynamic viscoelasticity measuring curves were obtained in the temperature range from -80 to 0°C at a heating rate of $1^\circ\text{C}/\text{min}$. DSC instrument used on the heat of fusion measurements was a SSC/5200(Seiko Denshi Instr., Tokyo, Japan). The sealed type sample pans were used. The weight was measured on a microbalance (Mettler-Toledo Ltd., Model MT5) accurate to $\pm 0.001\text{mg}$.

3. RESULTS AND DISCUSSION

Figure 2 shows typical dynamic viscoelasticity measuring curves of the storage modulus (E'), the loss

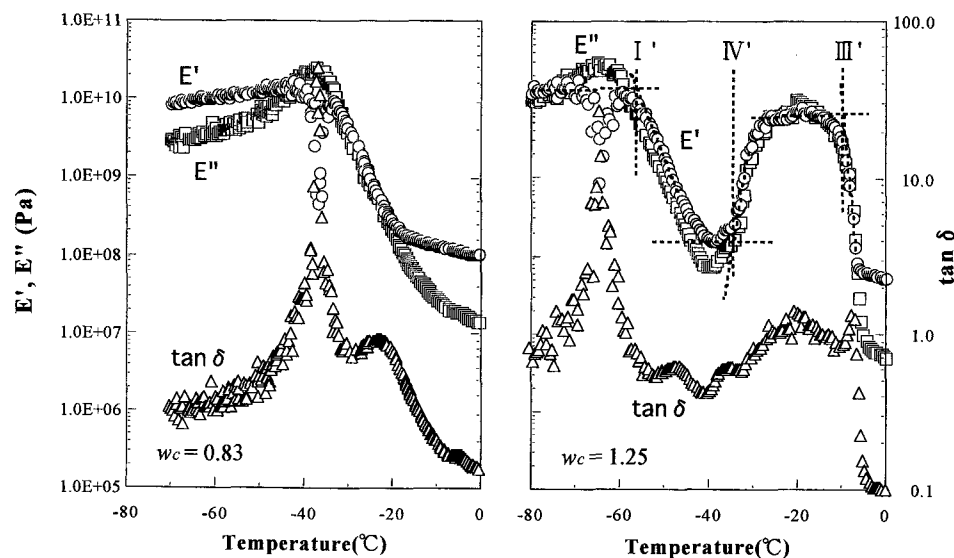


Figure 2. Typical dynamic viscoelasticity measuring curves of the storage modulus, E' ($\circ$), the loss modulus, E'' ($\square$), the loss tangent, $\tan \delta$ ($\triangle$) of NIPA(700mM) gel in the heating process with various water contents(from left to right, $w_c=0.83, 1.25$).

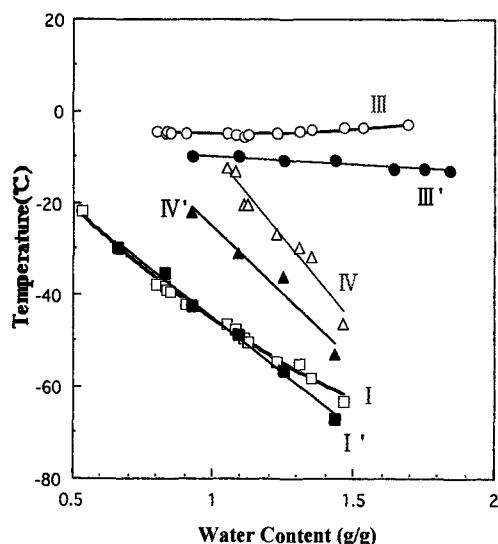


Figure 3. Comparison in the w_c dependence of transition point temperature obtained from the DSC thermograms (open symbols; I (□), II (◇), III (○), IV (△)) and from the dynamic viscoelastic measurement curves (closed symbols; I' (■), III' (●), IV' (▲)).

modulus (E''), the loss tangent ($\tan \delta$) of NIPA gel with various water contents. The w_c is 0.83 (left) and 1.25 (right). It can be seen that the NIPA gel indicated the complicated mechanical behavior by changing the temperature, as in the case of DSC measurements [11].

As shown in a figure 2(right), the inflection points, which appearing in the curve, are defined as follows; I', as a temperature where the E' begins to decrease (ca. -55°C in the case of $w_c=1.25$); IV', as a temperature where the E' begins to recover (ca. -35°C); III', as a temperature where the E' begins to decrease again (ca. -5°C). It is expected that the inflection point of E' curve corresponds with transition.

At the $w_c=0.83$, the E' dipped steeply around -37°C . At the same time, a sharp peak of the $\tan \delta$ is observed, and then E' decreases rapidly in the range from -32 to -20°C with increasing temperature. The E' curve at $w_c=1.25$ shows the behavior similar to that at $w_c=0.83$ from -80°C up to -40°C . The gradient of the E' curve in the range from I' to IV' temperatures is gentler than that above III' temperature.

We will compare above results with the DSC measurements in the following section [11]. Figure 3 shows comparison of transition point temperatures obtained from the DSC thermograms (shown open symbols; I, II, III, IV) and from the dynamic viscoelastic measurement curves (shown closed symbols; I', III', IV'). The I' temperature decrease gradually by increasing the water content up to $w_c=1.43$, and then disappears above it. The III' temperature is roughly constant at the w_c above 0.93. The IV' temperature is observed only within the range from $w_c=0.93$ to 1.43, and it decreases as w_c increases.

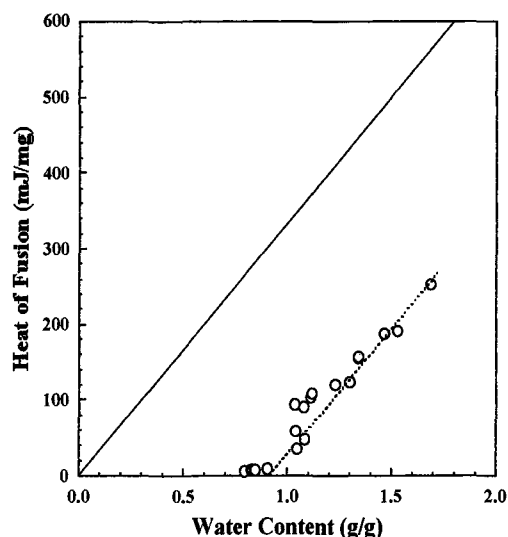


Figure 4. Plot of the enthalpy change versus water content calculated from the peak III area in DSC thermograms in the NIPA gel. The solid line is the theoretical line of the heat of fusion change when it is assumed that all the water in the sample freeze around 0°C into normal ice. The broken line is parallel to the theoretical line.

It disappears around $w_c=1.4$. The transition point of I' corresponds well to the results of DSC measurements.

From the above results, we would like to discuss the assignment of these phenomena. The rapid decrease of E' curve above I' temperature attributes to the glass transition, because the usual glass or amorphous materials changes from glassy state into soft rubbery state at the glass transition [13]. Moreover, the heat capacity gap I in the DSC thermogram was observed at the same temperature range. As can be seen from the figure, the behavior of the transition points III' and IV' are corresponding to those of the results of DSC measurements. It is thought that the steep decrease of E' curve above III' temperature attributes to the melting of the freezing water, because normal ice melts around 0°C . This phenomenon is supported further by the results of DSC measurements. In addition, it is thought that value of E' and E'' at about 0°C decrease with increasing w_c because of increasing the amount of water molecules as shown in figure 2. It is found that the steep increase of E' curve above IV' temperature attributes to the recrystallization of water, because the exothermic peak IV was observed in DSC. It means that these phenomena occurred because the water molecules in the gel developed interaction each other and recrystallized into crystallites at IV' temperature.

The endothermic peak III in figure 1 was observed within the range from -6 to -2°C in DSC thermograms. When water content increased to $w_c=0.8$, a small peak appeared. This peak area

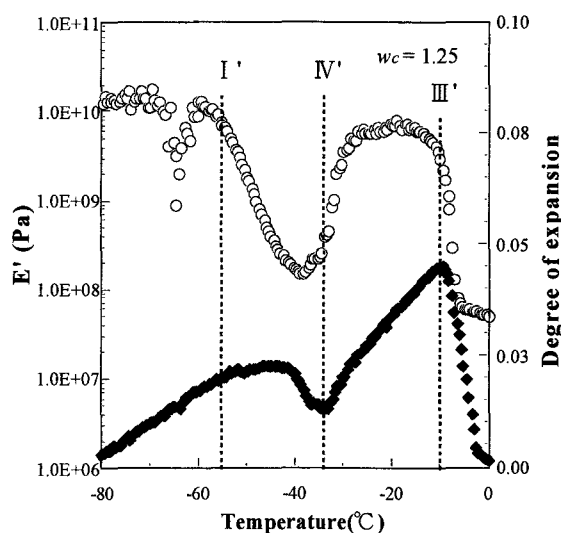


Figure 5. Temperature dependence of the storage modulus, E' (○), and the degree of expansion (◆) in the heating process of NIPA(700mM) gel in $w_c=1.25$.

increased with w_c above $w_c=0.8$, and becomes proportional to w_c . The transition enthalpy can be calculated from the peak area of each thermogram. Figure 4 shows a plot of the enthalpy change versus water content calculated from the peak III area in DSC thermograms in the NIPA 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 freeze around 0°C into normal ice. The broken line is parallel to the theoretical line. This fact indicates that the latent heat of fusion above $w_c=0.9$ is the same as that of normal ice. Thus, the water content where the heat of fusion became zero was 0.9mg for 1mg of dried sample. This point represents the water content having maximum quantity of bound water that may interact strongly with NIPA gel network. These results indicate that the numbers of water molecules per polymer segment are 5.7 for NIPA. It is thought that water molecules in the NIPA gel works mainly as a plasticizer below $w_c=0.9$.

Figure 5 shows the temperature dependence of the degree of expansion (◆) and the storage modulus, E' (○), in the heating process of NIPA gel in $w_c=1.25$. As can be seen from the figure, the slope of the curve for the degree of expansion becomes gentle higher than I' temperature and then decrease gradually by increasing temperature up to -34°C . Furthermore, it increases gradually in the range from IV' to III' temperatures and then decreases steeply above III' temperature. It means that gel is squeezed for compression above I' temperature, and then hardened by recrystallization at IV' temperature, moreover, expanded thermally in the range from IV' to III' temperature, and then soften by melting of water in heating process.

The marked change of degree of expansion was not observed at temperatures where the dip of E'

curve appeared. It is not clear from the present studies that the appearance of steep dip just before decreasing of E' at glass transition and melting of freezing water.

The present study strongly supports the results obtained from the DSC measurement. The detailed investigations by Raman spectroscopy and X-ray scattering experiments are now in progress.

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