

Effect of Moisture Absorption on Mechanical Properties of Dehydrated Gel

Nobuyasu Hiramatsu, Daisuke Ryu, Atsushi Namakura, and Kazuhiro Hara*

Department of Applied Physics, Fukuoka University,
Nanakuma, Jonan-ku, Fukuoka 814-0180

Fax: 81-92-865-6030, E-mail: hiramats@fukuoka-u.ac.jp

*Graduate School of Engineering, Kyushu University,
Hakozaki, Higashi-ku Fukuoka 812-8581

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

It is important to know the mechanical properties map as a function of temperature and moisture parameters, because it is sensitive to these ambient parameters even after the characteristic time (t_g') of the weight change in the dehydration process, and because the moisture absorbed might play a role of plasticizer, causing the shift of the loss tangent peak. In this paper, the visco-elastic behavior was examined under the moisture and temperature controlled condition for the gel samples whose water content is in the region of those after t_g' . The result is that, under constant temperature condition, the elastic modulus is gradually and then drastically decreases as the moisture increases and that the peak of loss tangent appeared around the moisture region of drastically decreasing modulus. This behavior is seemed to be ascribable to the primary dispersion. The softening vapor pressure and peak vapor pressure of loss tangent become higher as the temperature increases, which is elucidated by the hydrophilic nature of the network molecules at high temperatures.

Key Words: NIPA, Moisture Mechanical Properties, $\tan \delta$

1. Introduction

It is easy to imagine that the interaction between the network molecular chain and the solvent of water in a gel influences the elastic properties during the dehydration process. In fact, it has been reported¹⁾ that the peak of elastic loss tangent appeared around the characteristic time (t_g') where the gradient of the weight-time curve is altered in the dehydration process and that the amplitude of elastic stiffness increased up to 10^3 times the initial value after t_g' . The mechanical behaviour of almost completely dehydrated gel has also been investigated. From the frequency dependence of the relaxation phenomena, it is concluded that the dehydrated gel is classified into a normal polymer glass²⁻⁵⁾.

The dehydration process after t_g' must also be effected by the ambient moisture and temperature, because the equilibrium water content, which means the water content of the dehydrated gel at infinity of time period, is determined by these ambient parameters and because the mechanical properties are sensitively affected by the water molecules (moisture) absorbed from

the atmosphere. The moisture might be expected to play a role of plasticizer after t_g' , causing the shift of glass transition, even though the amount of the water adsorbed is very small. For the industrial and application field, such as storage of foods or biomaterials, these mechanical properties "map" as a function of these parameters should be the basic data and worth being clarified. However, the authors do not know the reports investigating such a map in detail.

When we suppose to make the temperature-scan experiment, which is one of the popular and easy ways to scan the experimental parameters, it is difficult to realize the constant humidity condition while the temperature is being scanned, because the vapor pressure corresponding to the given relative humidity is, of course, the function of temperature and accordingly the vapor pressure corresponding to the humidity is changed with the temperature. Therefore, in the case of investigating the mechanical properties after t_g' , it is not enough to use the instrument where only the temperature is controlled and it is unavoidable that the water content in the sample becomes less and less as

the temperature increases.

In this paper, the dynamic visco-elastic mechanical behaviour was investigated under moisture and temperature controlled condition for the dehydrated gel samples (N-isopropylacrylamide/sodium acrylate (NIPA/SA) copolymer) in the equilibrium state.

2. Experimental

The sample used in this study was N-isopropylacrylamide/sodium acrylate (NIPA/SA) copolymer gel, which was synthesized by a free radical copolymerization of NIPA (500mM) and SA (200mM) with a crosslinker (N,N'-methylene bisacrylamide), an accelerator (N,N,N',N'-tetramethylethylenediamine) and an initiator (ammonium persulfate) in water under nitrogen atmosphere. After the reaction, the gel was washed thoroughly with pure water to remove the residual chemicals. The gel was dehydrated very slowly for 2 weeks and was shaped in the size of 20 mm X 1.75 mm X 0.2mm for the dynamic visco-elastic measurements. The sample for the differential scanning calorimetry (DSC) was obtained from the same rump.

The dynamic visco-elastic measurement was carried out with DVA-225 (IT Keisoku Seigyō, Osaka, Japan). The distinguishing feature of this instrument is that the temperature and the moisture can be controlled independently up to 80°C and 95%RH. The moisture can be scanned linearly vs time while the temperature is

being kept constant. The measurement was carried out at the increasing rate of 1%RH per minute at a given temperature at 10Hz. We have checked that this rate is slow enough for the sample to attain the equilibrium state by monitoring the mechanical properties change by the stepwise increase and decrease of the moisture. The DSC Instrument used on the glass transition measurements was DSC120 (Seiko Instrument, Tokyo, Japan).

3. Results and Discussion

Figure 1 shows the vapor pressure dependence of the real part of dynamic modulus, E' . Each curve was obtained at each temperature shown in the figure. The modulus E' gradually and then drastically decreases as the vapor pressure increases. The vapor pressure where the drastic change occurs is called here "softening vapor pressure P_s ". The P_s increases as the temperature increases.

Figure 2 shows the vapor pressure dependence of the $\tan \delta$. The peaks are observed just above each P_s corresponding to the temperature. The peak position in pressure is named "peak vapor pressure P_p ". The P_p becomes higher as the temperature increases.

The relations of P_s and P_p vs temperature T are shown in Figure 3. The saturated vapor pressure vs T is also indicated as a reference in the figure. The plots are made $1/T$ as an abscissa and $\ln P$ as an ordinate. It

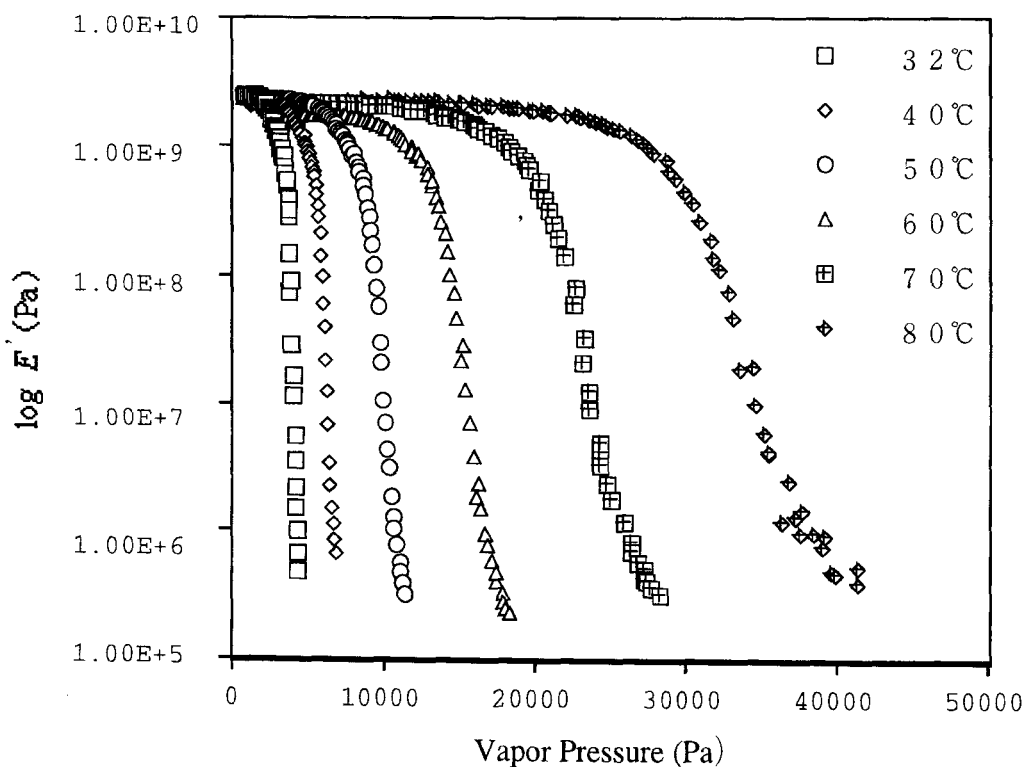


Figure 1 Vapor pressure dependence of dynamic elastic modulus E' at various temperature

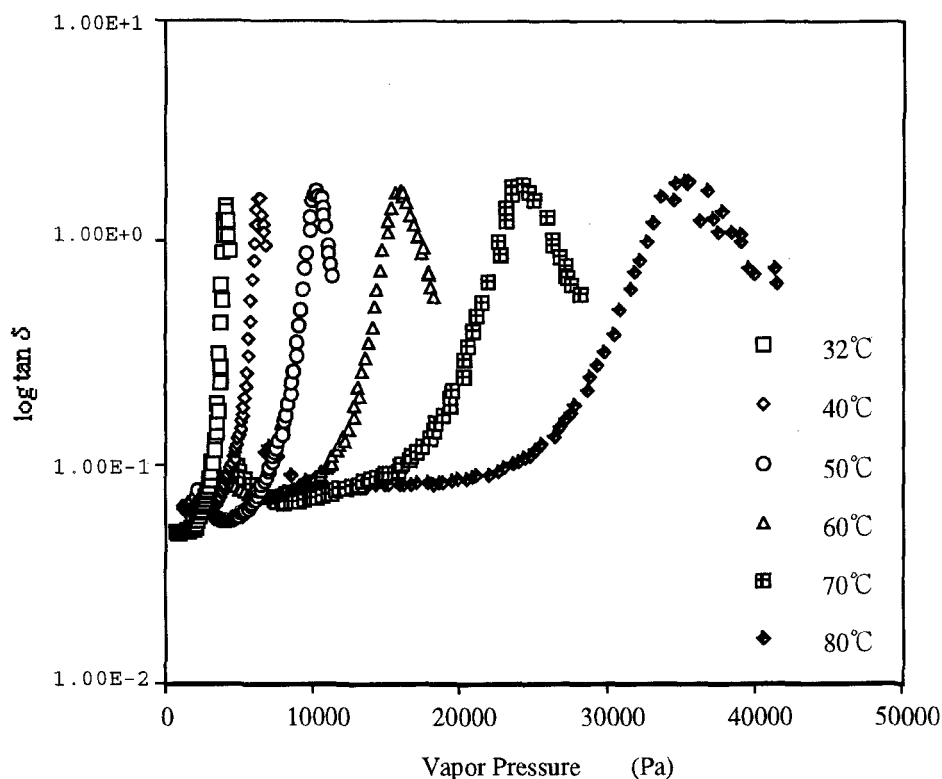


Figure 2 Vapor pressure dependence of $\tan \delta$ at various temperatures

is noted that the linear relations are observed and that the slope of the lines for P_s and P_p are almost the same and a little bit smaller than that of the saturated vapor pressure. It is interesting that these facts implies some "activation energy" model between two energy states. Further investigation is now being carried out.

The $\tan \delta$ peaks seem to be ascribable to the pri-

mary dispersion. Figure 4 shows the DSC thermogram of the same sample as the mechanical measurement in an open sample pan. The sample in an open pan loses water as the temperature increases, because the DSC instrument used here has no function to control the moisture and hence the relative humidity at high temperature becomes very low. We are convinced that

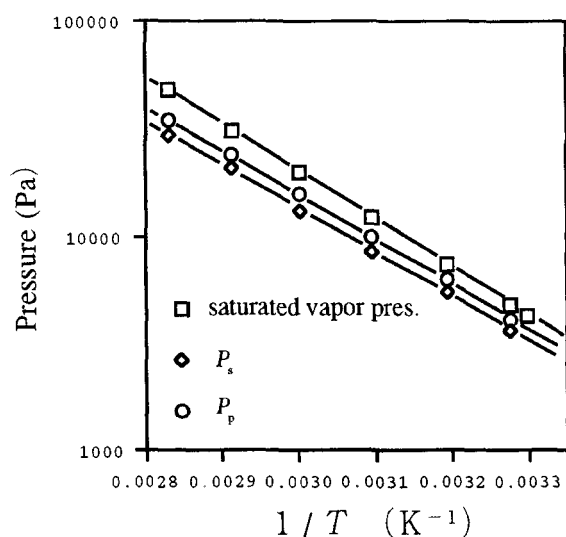


Figure 3 Temperature dependences of saturated vapor pressure, softening vapor pressure P_s , peak vapor pressure P_p .

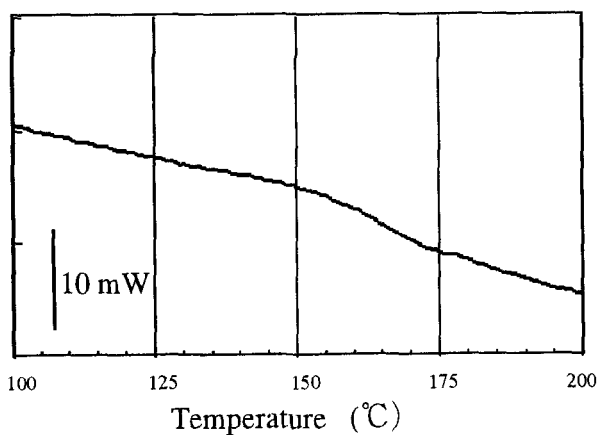


Figure 4 DSC thermogram of almost completely dehydrated NIPA/SA gel, showing the glass transition at about 162 °C.

the glass transition for extremely low water content sample occurs around 162°C.

The transition does not occur in the temperature range where the visco-elastic measurements were carried out, if the water content of the sample is extremely low. However, if the sample absorbs the moisture in the atmosphere, which makes the transition temperature lower, the $\tan \delta$ peaks can be observed even below 80 °C.

As mentioned before, the P_s and P_p become larger as the temperature increases. It is well known that NIPA molecular chains become more hydrophilic as the temperature increases, which is one of the cause of the volume transition⁶⁾. It may be reasonable that the dehydrated gel becomes soft at higher vapor pressure at higher temperatures, because the hydrophilic properties prevent the water molecules from entering into the network, hence the elastic stiffness stay hard till so many water vapor molecules reach the network. Figure 3 may show some kind of "antagonism" between the hydrophilic nature of the network chain and the water vapor molecules attacking.

It is necessary to carry out further investigation of the relation between the vapor pressure and water content in the gel. From these data, we can illustrate the mechanical properties map as a function of water content at various temperatures.

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