SHORT COMMUNICATIONS

Measurements of Mechanical Properties on a Swollen Hydrogel by a Tension Test Method

Yoshinori ISOMOTO OKA[†], Shuji SAKOHARA, Takehiko GOTOH, Takashi IIZAWA,
Kouhei OKAMOTO*, and Hirofumi DOI*

Department of Chemical Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

**Idemitsu Petrochemical Co., Ltd., 1-1 Miyamae, Shunan 745-8691, Japan*

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Characteristics of thermosensitive hydrogels are very attractive for uses of such as extraction, adsorption, actuator and drug-delivery systems by its reversible discontinuous large change in volume caused by a small change in temperature.^{1,2} The great abilities of functional hydrogels such as quick response and strict temperature dependence is very important in these applications. The structure of macroporous hydrogels achieves reversibly quick response between swelling and shrinking.^{3,4} Analyses on synthesis parameters and network formations enable the development of the greatly functional hydrogels. This development has been performed on the arrangements of a kind and concentration of cross-linking agents and of polymeric or synthetic processes.^{5,6} The investigation of mechanical properties contributes to the evaluation of macroporous structures. It is, however, very difficult to interpret the mechanical properties of hydrogels under different conditions of swelling degrees.

Methods to obtain strength or hardness (impression resistance) have been already developed in the fields of food and polymer gels.^{7,8} Compression tests have been also conducted to obtain elastic moduli in a few papers.^{3,9} Shearing moduli and visco-elastic shearing properties have been examined in papers.¹⁰ The conventional mechanical properties such as tensile strength, fracture strength and strain, and Poisson's ratio are especially important for the structural analyses and the use as component materials in practical services. These tensional mechanical properties have been hardly reported because of the low strength of swollen hydrogels and of difficulties of test methods.

The aim of this communication is to propose how to measure the tensional properties of the weak swelled hydrogels and to evaluate its mechanical characteristics. Poly(*N*-isopropylacrylamide) gel (NIPAm gel)

synthesized from copolymerization of *N*-isopropylacrylamide (NIPAm) with *N,N'*-methylenebisacrylamide (BIS) as a cross-linker was used as one of hydrogels having typically thermosensitive characteristics.

EXPERIMENTAL

The preparation of a gel was performed by radical polymerization. The concentrations of NIPAm and BIS were 2000 and 120 mol/m³, respectively. *N,N,N',N'*-Tetramethylethylenediamine (TEMED) and ammonium peroxydisulfate (APS) were used as the polymerization accelerator and initiator respectively. The polymerization temperature was 323 K, which was above the lower critical solution temperature (LCST, 305 K) of Poly(*N*-isopropylacrylamide). The NIPAm gel was formed in a sheet type cell with a thickness of 10 mm. The gel specimens were then cut in appropriate size for tension tests, and then put into water at given temperatures to keep swelling conditions. It is found from the SEM observation of the NIPAm gel that the macroporous structure composed of fine particles with a few micron size.

A schematic diagram of test procedures is shown in Figure 1. An accurate weight platform was utilized as a mass property system with RS232C interface connected with a computer. A specific jig was prepared to sustain the weak hydrogel specimens. A universal testing machine additionally supported the hanging up of the hydrogel specimens from a water pan at various water temperatures. The hanging up speed and room temperature were 0.33 mm/s and 293 K, respectively. Red marks as gauge were put parallel to transverse of the long specimen (see Figure 3). Appearances of the hydrogel specimen were observed with a digital camera during a tensile test in order to obtain local displace-

[†]To whom all correspondence should be addressed (E-mail: iyoshi@hiroshima-u.ac.jp).

Figure 1. Schematic diagram of a tensile (a hanging up) test method.

ment, width and a fracture point of the hydrogel. The local displacement around the fracture point was directly measured by an image processing to obtain strains, and the nominal stress was calculated with the variable load and the initial cross sectional area.

THEORETICAL CONSIDERATIONS

The weight platform indicates the weight of the pan, the jig, water and of an immersed gel in the water, in the first stage of the hanging up test. When the gel specimen is hanged up and exposed in the air at room temperature, the indicated weight (load) by the platform decreases with the hanging up due to the release of the buoyancy. From the load balance, the sum of the load L_G acted at the fracture point (F.P.) and the load L_P indicated by the weight platform is equal to the weight of the volume V under the point to be fractured in the last stage, as shown in Figure 1 and eq 1.

$$L_G + L_P = \rho g V \quad (1)$$

where ρ is the density of the tested gel and g is gravitational acceleration. As the load L_G is also expressed with the immersed volume V' and the density of water ρ_w as eq 2, the weight by the platform indicates the buoyancy of the immersed volume $\rho_w g V'$ as shown in eq 3.

$$L_G = \rho g V - \rho_w g V' \quad (2)$$

$$L_P = \rho_w g V' \quad (3)$$

When the gel specimen is hanged up and further exposed by ΔV , the increased load ΔL_G is given by

$$\begin{aligned} \Delta L_G &= \{\rho g V - \rho_w g (V' - \Delta V)\} \\ &\quad - \{\rho g V - \rho_w g V'\} = \rho_w g \Delta V \end{aligned} \quad (4)$$

Then a local part of the gel over the water level suffers the load which corresponds to the buoyancy on the part of the gel between the position and the water level. Therefore, the load acted at the point of the subsequent fracture is equal to the buoyancy on the exposed gel volume below the fracture point. The weight of the jig and the upper part of the gel from the fracture point is nearly constant after the hanging up over the fracture point, and therefore considered to be an offset load. The geometrically smooth curve of the specimen makes the narrow part of the central specimen reasonably fractured without any irregular stress concentration.

RESULTS AND DISCUSSION

Figures 2 and 3 show an example of the change in weight measured by the platform versus testing time and appearances of the gel at the several points of the testing time in a hanging test. The minute weight change in an order of mN greatly increases with the release of buoyancy of the exposed parts from the water level. The upper part of the specimen with the jig is just over the water level at the point of A (40 s). The point B (50 s) shows that the water comes down, which was once pushed up by the surface tension of water. The weight change gradually increases with the hanging up of the gel specimen, and suddenly decreases at the point C (350 s) by a fracture followed by the drop of the specimen.

Beyond the point B, the relation between the apparent stress, which means the indicated weight change divided by an initial area of cross section at the frac-

Figure 2. Weight change vs. testing time plots measured by a hanging up testing of the immersed gel specimen.

Figure 3. Appearances of a hydrogel specimen during a hanging up testing.

ture point, and the local strain around the same point is shown in Figure 4a. It can be seen that the apparent stress gradually increases with the strain and that the gel specimen is fractured at a strain of 0.7. The high value (*ca.* 6000 Pa) of the initial apparent stress implies that the load measured by the platform includes the buoyancy of the upper part of the gel specimens and the jig. Nominal stress can be therefore obtained to subtract the initial apparent stress from a given stress as shown in Figure 4b. The curve was not affected by strain rate or hanging up speed in another tension test.

The nominal stress-strain diagrams of the NIPAm gel at various water temperatures are shown in Figure 5. The curves were not linear and shifted depending upon the temperature. The stress-strain curves were concave and nearly same, at low water temperatures

from 279–296 K. It seemed that water in the pores of the hydrogel was disgorged and the pores were squeezed in the small strain region. The hydrogel was, therefore, considered to be easily deformed by the small stress. Thereafter the resistance of tensile stress increased with the increase in strain because of a little shrinking due to the higher room temperature than water one. At high temperatures of 313 and 323 K the initial stress curves were convex. This behavior seemed to be caused by low internal tensions of the swollen networks of the hydrogel due to the drop of the gel temperature to the room one during the hanging up of the hydrogel. The curves at temperatures of 299 and 303 K are probably in a transition region of the gel temperature. On the other hand, the fracture strength increased with the increase in temperature. This is due to the increased gel density

Figure 4. An apparent and a nominal stress vs. strain curve in a hanging up testing.

accompanied by the shrinking of the gel. From the fact that the displacement of the gel before fracture was perfectly released by de-loading, the elastic deformation is definitely followed by the fracture in spite of the non-linear curves.

The dependence of temperature on a representative elastic modulus, which was the slope at a high strain region in Figure 5, was shown in Figure 6. A temperature of 305 K is the LCST of poly NIPAm so that the NIPAm gel is gradually shrunk as increased with temperature and constantly shrunk over the LCST, as the swelling degree³ are also shown in Figure 6. The behavior of the swelling degree means the change in density or volume of the hydrogel affected by the temperature. The behavior of the elastic modulus is found to well relate to the swelling degree except for the region below room temperature (R.T.). The elastic modulus below R.T. was nearly constant. It is reasonably suggested that the hydrogel swelled in the water at the low temperature was shrunk by R.T. during the hanging up. The elastic modulus of the hydrogel is considered to depend upon the density of the networks and swollen conditions.

The mechanical properties of the hydrogel are listed in Table I. The average elastic modulus means the fracture strength divided by the fracture strain. This type of the hydrogel showed a sudden fracture at a

Figure 5. Nominal stress vs. strain curves in a hanging up testing.

Figure 6. The dependence of temperature on a representative elastic modulus and a swelling degree.

strain from 0.6 to 0.7 after the elastic deformation at any temperatures. The fracture strain depends upon a concentration of a cross-linker and synthesizing conditions. The Poisson's ratio was high with *ca.* 0.5 at an initial stage of a tension test (low strain), and reached constant values of 0.3–0.35 independent of temperature under the various test conditions, as listed in Table I. It is probably attributed to the reduction of a cross sectional area by the squeezed pores predominantly caused with the stretch of the gel networks. These values are unexpectedly smaller than those of

Table I. Mechanical properties of a NIPAm gel

Temperature / K	279	283	293	296	299	303	313	323
Fracture Strain / —	0.63	0.65	0.70	0.67	0.70	0.67	0.61	0.60
Fracture Strength / Pa	3360	3590	3740	3650	4900	10800	11500	13600
Average elastic modulus / Pa	5330	5520	5340	5450	7000	16100	18900	22700
Poisson's Ratio / —	0.30	0.34	0.34	0.34	0.33	0.35	0.33	0.30

common polymers and non-porous gels.

A new testing method to obtain tensional mechanical properties of hydrogels was proposed in this study. Tensional elastic modulus, fracture strength and strain, and Poisson's ratio, which are inevitable but very unobtainable for structural and functional design of thermosensitive hydrogels, could be evaluated in the tension tests. Both the elastic modulus and the fracture stress of the NIPAm gel were shifted with test temperatures depending upon the conditions of the gel networks and swelling (or shrinking). The fractured strains were 0.6–0.7 and Poisson's ratios 0.3–0.35 respectively in this case of NIPAm with BIS of 120 mol/m³. This method leads to important discussion of porous hydrogel networks and mechanical properties and knowledge of properties for material design. Further results should be obtained on various types of hydrogels.

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REFERENCES

1. R. F. S. Frettas and E. L. Cussler, *Chem. Eng. Sci.*, **42**, 97 (1987).
2. Y. Seida and Y. Nakano, *J. Chem. Eng. Jpn.*, **29**, 767 (1996).
3. T. Gotoh, Y. Nakatani, and S. Sakohara, *J. Appl. Polym. Sci.*, **69**, 895 (1998).
4. Y. Tomotake, Y. Maeda, T. Gotoh, and S. Sakohara, *Kobunshi Ronbunshu*, **59**, 44 (2002).
5. T. Gotoh and S. Sakohara, *Recent Res. Dev. Macromol. Res.*, **3**, 77 (1998).
6. Y. Tomotake, Y. Maeda, T. Himeno, and S. Sakohara, *Kobunshi Ronbunshu*, **59**, 438 (2002).
7. J. P. Gong and Y. Osada, *Prog. Polym. Sci.*, **27**, 3 (2002).
8. S. Sakohara, H. Takioka, T. Nikai, and K. Takatani, *Kagaku Kogaku Ronbunshu*, **29**, 62 (2003).
9. C. Sayil and O. Okay, *Polymer*, **42**, 7639 (2001).
10. D. M. Ole Kiminta, P. F. Luckhan, and S. Lenon, *Polymer*, **36**, 4827 (1995).