JOURNAL OF MATERIALS SCIENCE 32 (1997) 491–496

Properties of hydrogels synthesized by freezing and thawing aqueous polyvinyl alcohol solutions and their applications

YOSHIHIRO MORI, HITOSHI TOKURA, MASANORI YOSHIKAWA
Yoshikawa laboratory, Department of Control and Systems Engineering, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152, Japan

The hydrogel synthesized by freezing a polyvinyl alcohol (PVA) aqueous solution and thawing it slowly has high water content, excellent mechanical properties of high tensile strength, elongation and good shape recovery by elasticity. The PVA used had a degree of polymerization of 2500 and a degree of saponification of 99.5 mol% . The solution was obtained by dissolving 7.5 g of PVA in 80 g of water, this was frozen at $-50\,^{\circ}C$ for 3 h and then warmed up to room temperature over 10 h. This freezing–thawing process was repeated once again and a hydrogel was synthesized. The hydrogel had a water content of about 90 wt% . Its tensile strength was 0.6 MPa and the elongation at break was 130% . The shape of the hydrogel which was deformed by an external force recovered in a short time when it was released from the force. This recovery had good persistence and repeatability. Applying these properties a strain sensor and a gas pressure sensor were tested. Furthermore, a PVA hydrogel rod containing polyacrylic acid was used as a bending actuator. This hydrogel had the ability to deform when direct current was applied.

1. Introduction

Polymer gels have attracted attention as "intelligent materials" because of their peculiar material forms. They also have been studied in every field. However, their practical use is mainly limited to applications of high water absorption because gels have inferior mechanical strength. Indeed gels become stronger with cross-linking, but there is the possibility that the flexibility and the water content decrease. Lately, it has been shown that hydrogels with high water content, strength and elasticity can be synthesized easily by repeatedly freezing and thawing a concentrated (more than 5%) aqueous solution of polyvinyl alcohol (PVA) with a high degree of saponification (more than 98 mol %), without any chemical processing [1]. Such advanced hydrogels are expected to find application in areas which were unsuitable for gels developed in the past because strong external force operates them.

This paper describes mechanical properties such as tensile strength and the shape recovery by the elasticity, and the water content as well as describing potential application areas.

2. Sample PVA hydrogel

The PVA hydrogel used in this study was synthesized as follows: 7.5 g of PVA with a degree of polymerization of 2500 and a degree of saponification of 99.5 mol % was dissolved in 80 g of water with heating, and a uniform aqueous solution was obtained. After pouring into a mould with the desired shape, it was frozen at $-50\,^{\circ}C$ for 3 h. The frozen solution was warmed up to room temperature over 10 h and the PVA hydrogel was obtained. The hydrogel which was synthesized by repeating the freezing and thawing process twice, is denoted in this paper as the "sample hydrogel".

Fig. 1 shows the appearance of a sample hydrogel synthesized in the form of a membrane. It looks white and opaque, and it has an elastic feel to it with flexibility like jelly. The state of the hydrogel is thought to be a three-dimensional network structure which is constructed by semi-crystallites of hydrogen bonds of PVA polymer filled with a solvent [2]. A secondary electron microscope photograph of the sample which was dried by the critical point drying technique is shown in Fig. 2. It is clear from this figure that it has a microporous structure. Heating to higher than about $60\,^{\circ}C$ causes it to melt back into the aqueous solution because of the dissociation of hydrogen bonds. If the frozen solution of PVA is warmed up fast, the hydrogel is sticky, colourless and transparent (Fig. 3). In addition, though the thawing time also affects the mechanical properties, the freezing time does not.

0022–2461

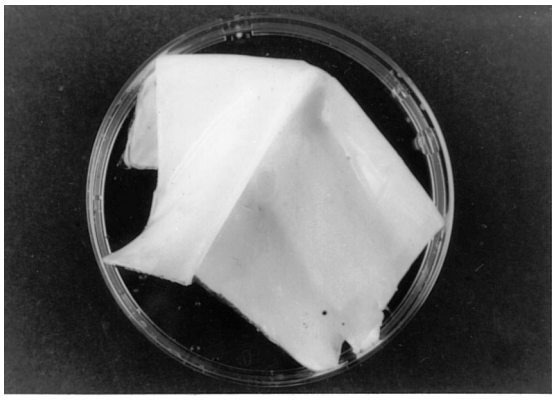


Figure 1 Sample PVA hydrogel.

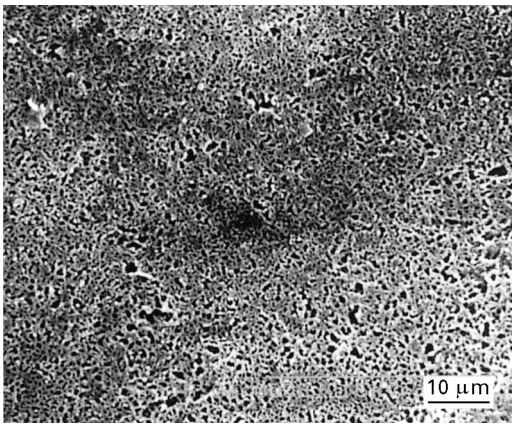
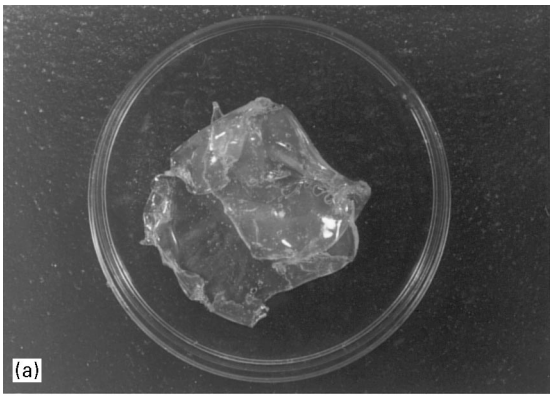


Figure 2 SEM photo of the surface of the sample PVA hydrogel.



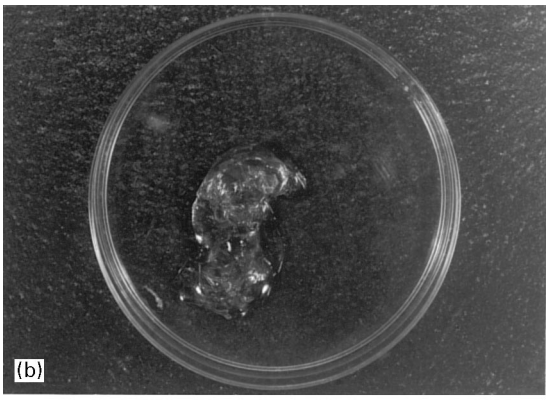


Figure 3 The influence of the thawing time on PVA hydrogels: (a) 3 h and (b) 10 min.

3. Properties of the sample PVA hydrogel

3.1. Water holding ability

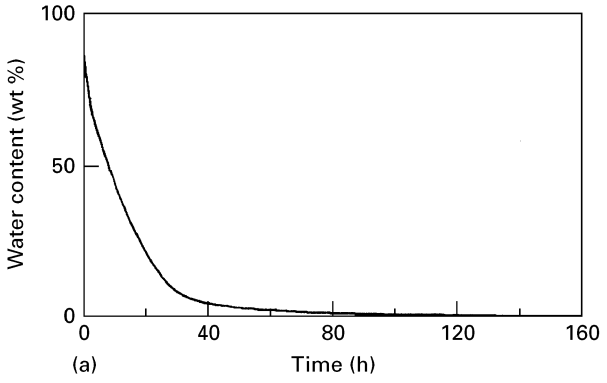
The weight of a sample hydrogel before and after drying were compared to measure the water content. It had a high water content of about 90 wt %. To investigate the water holding ability, a sample hydrogel of 50 mm long, 20 mm wide and 0.5 mm thick was subjected to conditions of 14.8 °C in temperature, 76% in humidity and no out flow. The result is shown in Fig. 4. Fig. 4a shows the change over a long period of time. It takes more than 140 h to become completely dried. Thus the sample is found to have a high water holding ability. Fig. 4b shows change during the first hour. The decrease of the water content is at most 0.5 wt% per 30 min, in a word, slow.

The sample hydrogel got smaller and harder when it was dried. The dried gel was colourless and transparent. The dried gel did not revive in water to its original state. Drying seems to cause changes to the bonding of the polymers.

3.2. Tensile strength

Next, mechanical properties of the PVA hydrogels were evaluated by measuring the tensile strength. The size of the test pieces were 90 mm long, 10 mm wide and 0.7 mm thick, with a gauge length of 60 mm. Tensile tests were performed by fixing the upper part of the sample and hanging weights on its lower part.

Time to thaw the frozen PVA aqueous solutions affects the mechanical strength of the hydrogels. To investigate the effects, hydrogels subjected to 10 h to



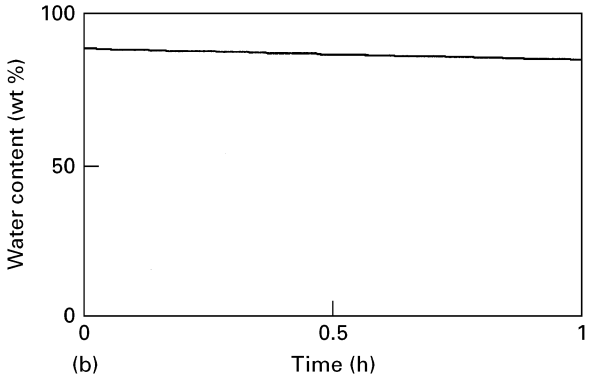


Figure 4 Relationships between time and water content of sample PVA hydrogel. (a) Changes over long time period. (b) Changes during the first hour.

3 h and 10 min thawing with one freezing–thawing process were tested. Fig. 5 represents the tensile–strain curves The hydrogel subjected to 10 min thawing is found to be mechanically very weak. The hydrogel subjected to 3 h thawing improved in tensile strength and elongation. The hydrogel subjected to 10 h thawing especially improved in strength in spite of the decrease in elongation. In short, the more slowly the frozen PVA solutions thaw, the stronger the hydrogels become. The reason is supposed that crystallization of semi-crystallites constructing a three-dimensional network structure is promoted by slow thawing [2].

The effects of the number of freezing–thawing processes were investigated, and the results are represented in Fig. 6. The thawing time for each test piece was 10 h. This figure shows that the sample hydrogel, prepared by repeating twice the freezing–thawing process, has high tensile strength and elongation at break of 0.6 MPa, and 130%, respectively. It also shows that the tensile strength of hydrogels decreases with decreasing numbers of the freezing–thawing processes, and the elongation decreases with increasing freezing–thawing processes. These results suggest that repetition of the processes makes the bonding of the polymers closer.

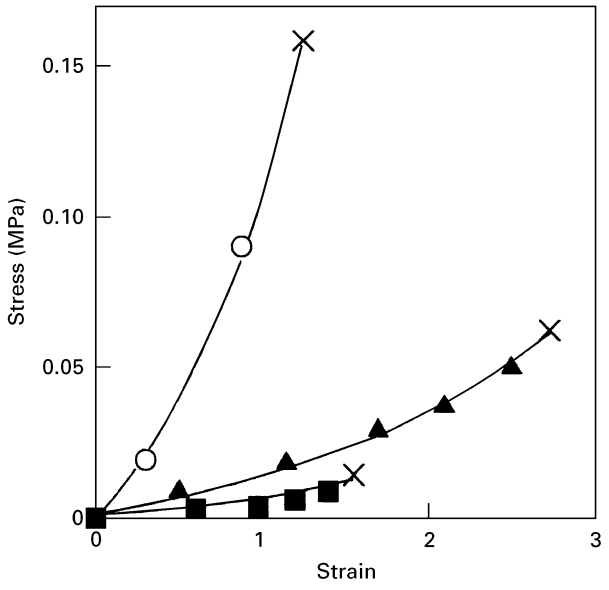


Figure 5 Stress–strain curves under the influence of thawing time (○ 10 h; ▲ 3 h; ■ 10 min).

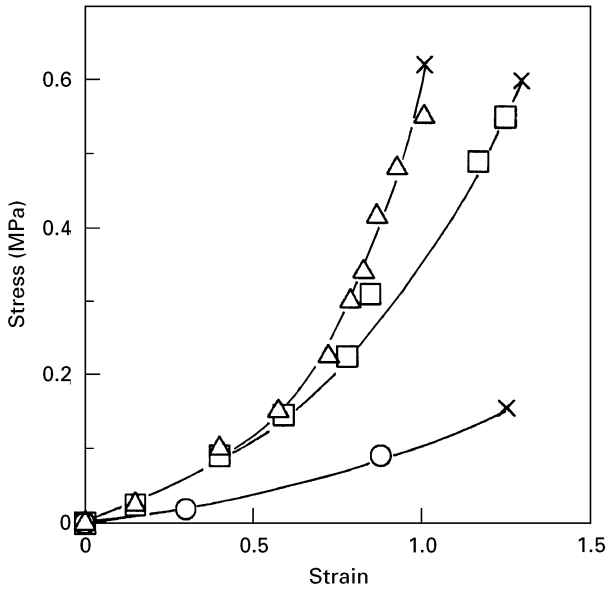


Figure 6 Stress–strain curve under the influence of the number of freezing–thawing processes (○ once; □ twice; △ 3 times).

3.3. Shape recovery by the elasticity

The sample hydrogel not only has high tensile strength and elongation but also flexibility and elasticity. It is expected that it recovers its shape well after deformation by an external force. Hence shape recovery was investigated.

The method is as follows. The solvent of a sample hydrogel was exchanged for an electrolyte solution. Then platinum electrodes were attached to the hydrogel containing the electrolyte. The recovery was investigated by measuring the electrical resistance of the hydrogel from the beginning of the deformation to the end of the recovery. It was expected that the electrical resistance of the hydrogel containing an electrolyte solution would change when the hydrogel was deformed because of the deformation of the current path and that it would return to its original value when the shape recovered

Three sample hydrogels, 90 mm long and 0.7 mm thick, were soaked in 0.02 N NaOH aqueous solution to exchange the solvent. The width of the sample hydrogels were 7, 5 and 3 mm, respectively. Aqueous NaOH does not affect the properties of the hydrogels. The presence of aqueous NaOH in the hydrogels is considered to be like that of water because this solution is not concentrated and its viscosity is almost the same as water. To confirm the change of the electrical resistance by deformation, clip-type electrodes were attached to the hydrogels 80 mm apart as shown in Fig. 7, and the resistance was measured when the

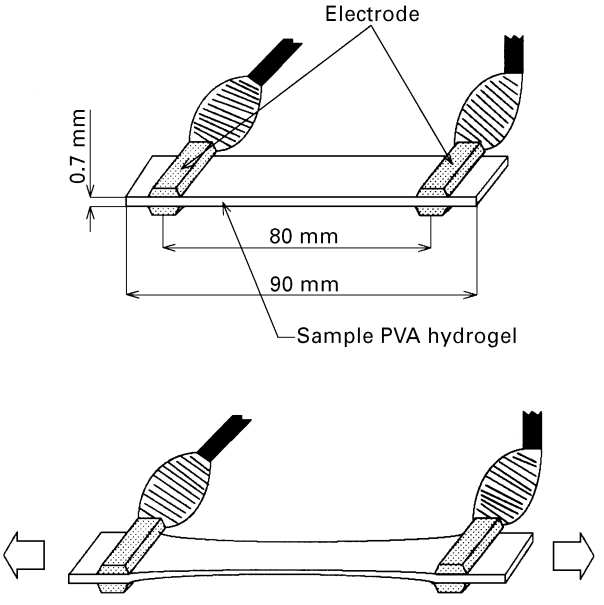


Figure 7 Stretched hydrogel with electrodes.

hydrogels were stretched. The frequency of the applied current was 1 kHz to avoid changing the resistance by electrolysis of the solution. Fig. 8 represents the relationship between the strain and the electrical resistance. It is clear that the resistance increases with increasing strain. This is because the distance between the two electrodes lengthens and the cross-section of the hydrogel decreases when it is stretched. After measurement when the hydrogel was released, the resistance returned to the value before stretching. From these results the behaviour of the change of electrical resistance due to deformation was confirmed. Thus this was a suitable evaluation method.

Next, the shape recovery was investigated. A sample hydrogel of 50 mm long, 20 mm wide and 0.5 mm thick was soaked in 0.02 N NaOH aqueous solution. After that, two clip-type electrodes were attached 40 mm apart as shown in Fig. 9. The change in resistance was

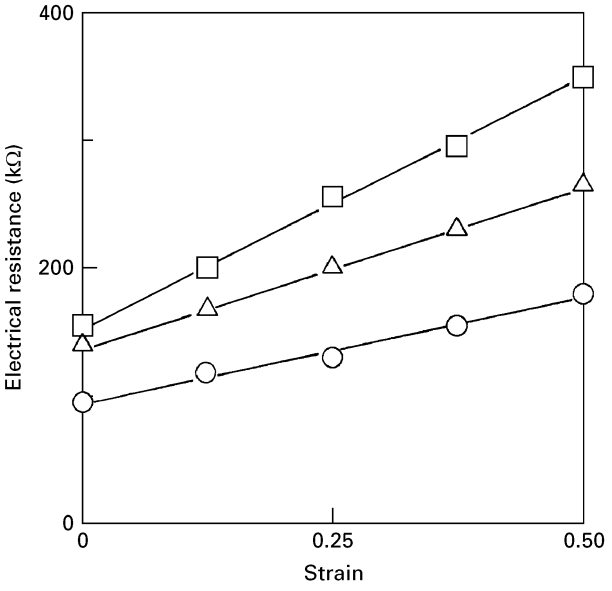


Figure 8 Relationships between strain and electrical resistance of sample hydrogel containing 0.02 N aqueous NaOH. Width: ○ 10 mm; △ 7 mm; □ 5 mm.

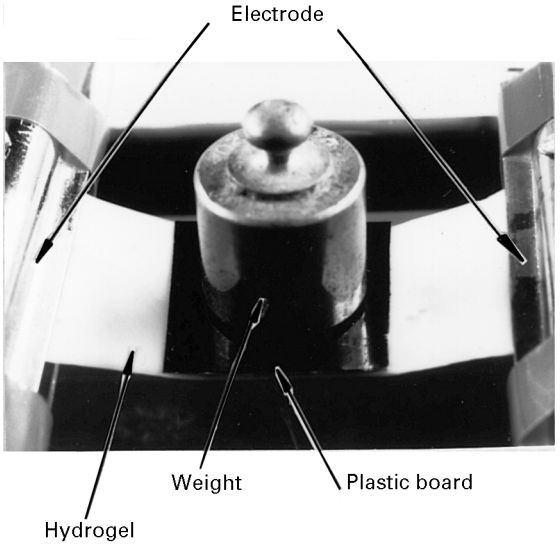


Figure 9 Measurement of shape recovery.

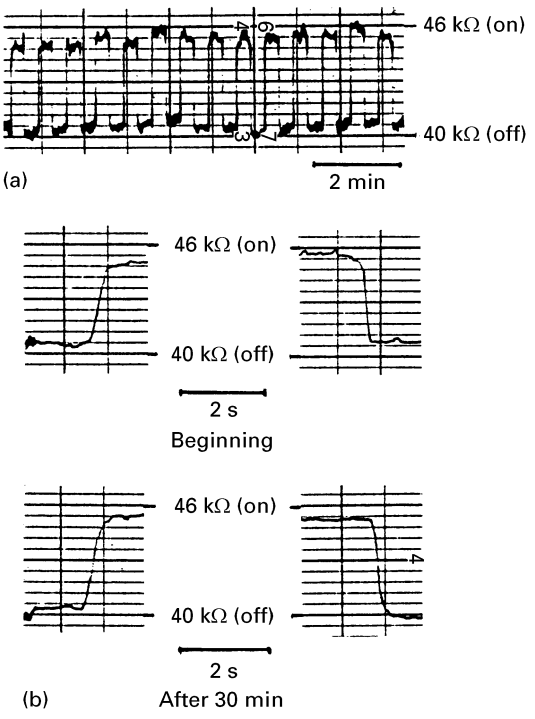


Figure 10 Shape recovery measured by electrical resistance when the weight was put on or removed: (a) repeatability; and (b) responses.

measured when a weight of 50 g was put on and removed from the plastic board of negligible weight on the hydrogel. Fig. 10 represents the changes observed when the weight was put on and removed repeatedly at 20 s intervals. The value of the resistance is 40 kΩ when the weight is not on the hydrogel, and 46 kΩ when on. Fig. 10a shows the repeatability. These responses continue for more than 30 min. It is clear from this result that the sample recovers its shape well. Fig. 10b and c show the responses at the beginning of the measurement and that after 30 min. The response times are 0.5 s in both measurements, i.e. the shape recovers in 0.5 s. From the above, it can be said that the sample hydrogel has the ability to recover its shape in a short time, and in addition, has excellent persistence and repeatability of the recovery.

4. Application of the properties of the PVA hydrogel

4.1. Application to sensors

As mentioned above, the sample hydrogel has high water holding ability, tensile strength and shape recovery after deformation. Thus the properties of the hydrogel were applied to sensors. The hydrogels shown in Fig. 7 can be used as strain sensors since the electrical resistance increases with increasing the strain as shown in Fig. 8 and the responses are satisfactory. They are expected to sense the motion of the body on account of their high elongation and easiness of fitting the skin. If the hydrogel is uncoated, there is the possibility that the electrical resistance could be changed by evaporation of the solution. But the sensors are considered to be able to be used for at least 30 min on the basis of the results shown in Fig. 4. The

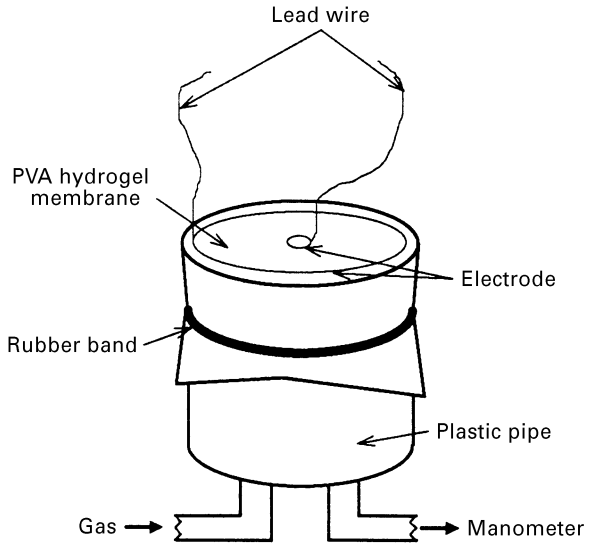


Figure 11 Gas pressure sensor.

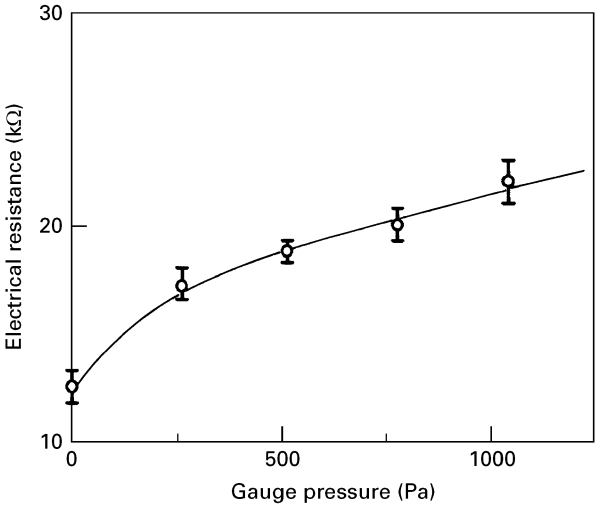


Figure 12 Relationship between gauge pressure of the gas and electrical resistance of the hydrogel membrane.

hydrogel could also be applied as a pressure sensor by using it as a diaphragm. The hydrogel membrane of 0.2 mm thick containing the electrolyte solution was stretched on a cylinder having an inside diameter of 40 mm and outside diameter of 45 mm. Ring-shaped platinum electrodes having diameter 42 and 10 mm, respectively, were attached to the membrane (Fig. 11). The pressure in the cylinder was raised by pumping air into it, and the relationship between the gauge pressure in the cylinder and the electrical resistance was measured. Fig. 12 shows the results. The resistance increases with increasing pressure because the membrane is stretched. The linearity of the relation is somewhat inferior, and dispersion exists around each point, but it has the ability to sense a gas pressure of at least 1 kPa.

4.2. Application to actuators

The behaviours of the PVA hydrogels containing an electrolyte solution were described above. This paragraph concerns hydrogels containing polyelectrolytes. When a PVA aqueous solution containing polyacrylic acid (PAA) is first frozen and then thawed slowly, a hydrogel like the PVA sample hydrogel is obtained [3]. In this case, the PVA is not affected by the PAA because no chemical reactions occur. The construction of the hydrogel is considered to be that PAA polymers penetrate into the PVA polymer network. Polyelectrolytes can stay in the hydrogel in contrast to the electrolyte solution so a PVA hydrogel having the properties of PAA is expected to be obtained and it seems possible that it might be deformed by an electric field in an electrolyte solution [4] or by application of direct current (d.c.) [3]. The behaviour of the former have already been elucidated [5], so in this study, the behaviour of the latter are studied.

A PVA hydrogel rod containing PAA with platinum wire electrodes having 0.1 mm diameter (shown in Fig. 13) was prepared. The hydrogel was synthesized as follows: 7.5 g of PVA was dissolved in 50 ml of 30% dimethyl sulfoxide–70% water solvent by heating. 30 g of the 25% polyacrylic acid with a degree of polymerization of 8000–12 000 was added to this solvent. After that, the freezing and thawing processes were performed in the same manner as described for the sample PVA hydrogel. Wire electrodes were set before freezing. The obtained hydrogel (named PVA–PAA hydrogel) rod with electrodes were soaked in 0.02 N NaOHaq and d.c. was applied to the electrodes. As a result, the rod became bent with the anode side inside as shown in Fig. 14 by shrinkage of the hydrogel near the anode. The reason is considered to be that the distribution of the pH in the hydrogel changes by the movement of ions [6]. When d.c. was

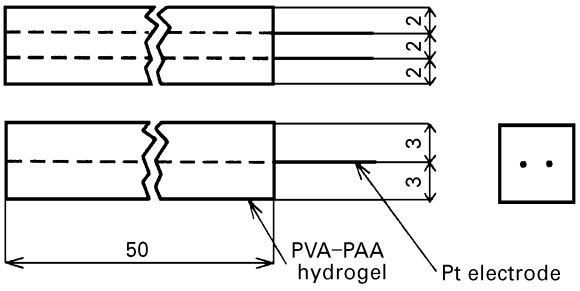


Figure 13 PVA–PAA hydrogel rod with Pt electrodes.

Figure 14 Bending of the PVA–PAA hydrogel rod.

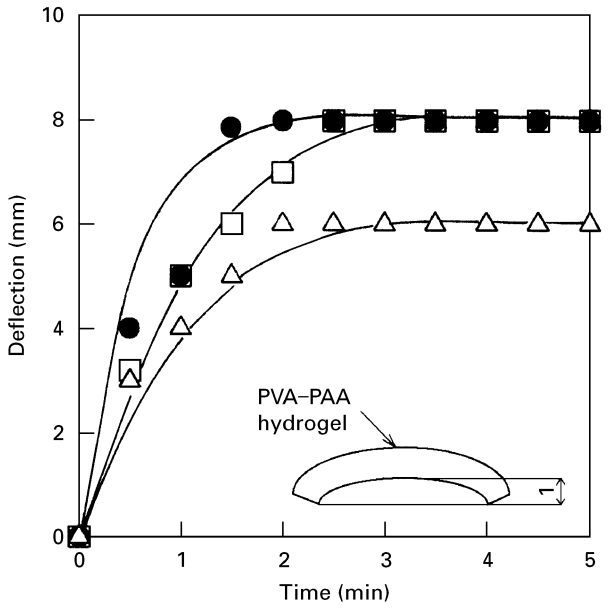


Figure 15 Relationships between deflection and applied voltage (△ 10 V; □ 15 V; ● 20 V).

applied, water was electrolysed at the electrodes:

$$\text{(Anode)}\ 2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (1)$$

$$\text{(Cathode)}\ 2H_2O + 4e^- \rightarrow 2OH^- + H_2 \quad (2)$$

H^+ ions near the anode decrease the degree of dissociation of carboxyl groups and the electrostatic repulsion of PAA polymer's decreases. As a result, shrinkage occurs and the rod bends. Na^+ ions in the hydrogel are drawn to the cathode and OH^- ions distribute near it to maintain the neutrality of the hydrogel. This behaviour does not occur in the PVA hydrogel. The relation between the deflection and applied voltage are represented in Fig. 15. The rods bend faster with increasing voltage because the electrolysis shown in Equations 1 and 2 is promoted. If the polarity of applied d.c. is reversed, the bent rod can stretch. And it can bend out of the aqueous NaOH solution. In addition, it is not destroyed by the repeated bending. This bending behaviour requires a long response time, but the rod is considered to be an actuator and a structure. This can be applied to the finger of the gripper, and flexible grippers are expected to be obtained with PVA–PAA hydrogel rods.

5. Conclusion

It has been found that the hydrogel synthesized by freezing a PVA aqueous solution and thawing it slowly has a high water content, excellent mechanical properties of high tensile strength, elongation and shape recovery, and that it has the ability to be applied as a sensor when it can interact with the external force. For example, it can be applied as the strain sensor or a gas pressure sensor using the hydrogel containing an electrolyte solution. The PVA hydrogel rod containing PAA with platinum wire electrodes can bend under application of d.c. This rod is able to be applied to fingers of a gripper as a flexible actuator by this bending behaviour.

References

1. M. NAMBU, *Kobunshi Kakou Jpn.* **32** (1983) 523.
2. S. H. HYON, W. I. CHA and Y. IKADA, *Kobunshi Ronbunshu* **46** (1989) 673.
3. T. SHIGA, Y. HIROSE, A. OKADA and T. KURAUCHI, *J. Appl. Polym. Sci.* **44** (1992) 249.
4. T. SHIGA and T. KURAUCHI, *J. Appl. Polym. Sci.* **39** (1990) 2305.
5. Y. OSADA and M. HASEBE, *Chem. Lett.* (1985) 1285.
6. Y. HIROSE, *Kobunshi* **37** (1988) 746.

Received 20 October 1995
and accepted 17 September 1996