Effect of Chemical Cross-linking under Elongation on Shape Restoring of Poly(vinyl alcohol) Hydrogel

TOSHIHIRO HIRAI,* HIDETOSHI MARUYAMA, TAKASHI SUZUKI, and SADAO HAYASHI

Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda-shi 386, Japan

SYNOPSIS

An anisotropically swollen hydrogel of poly(vinyl alcohol) (PVA) was found to be able to restore an isotropic physical shape by restoring isotropic physical cross-links induced by anisotropically distributed chemical cross-links. The anisotropic chemical cross-links were introduced in the isotropic physical gel by cross-linking with glutaraldehyde under elongation. The physical gel was made from the PVA aqueous solution by repetitive freezing and thawing. The chemically cross-linked gel had kept its original shape and physical properties despite the chemical treatment under strain. However, by the heat treatment in boiling water, the gel changed its form anisotropically depending on the strain applied in the chemical treatment. The anisotropically swollen gel was deswollen in methanol and then reswollen in water. The reswollen gel took back its original isotropic shape, suggesting that the anisotropic chemical cross-links thus introduced in the gel have a memory effect on the restoration of isotropic physical cross-links. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Highly elastic hydrogel of poly(vinyl alcohol) (PVA) has been known to be prepared by repetitive freezing and thawing of an aqueous solution of PVA.[1] The elastic hydrogel has been investigated from various standpoints, for instance, as a material for membrane whose separability is controllable by operating pressure.[2] The hydrogel has also been investigated as a possible candidate for artificial muscle or gel actuator, since it has enough toughness and response rate on swelling and/or deswelling.[3-5] As the gel is biologically inactive and has good biocompatibility, it has been applied for medical uses or a matrix for enzyme immobilization.[6-8]

We have been investigating the effect of network structure on the contraction behavior of the gel as an artificial muscle.[3] In the course of the study, we found that the PVA hydrogel has a shape-memorizing property, i.e., the gel could fix ca. 200% of strain without losing elastic property.[9] The fixed strain could be released instantly by immersing the gel into hot water.

In this communication, we are going to show another interesting property on shape restoring of the gel, i.e., the gel could restore the isotropic physical shape by restoring the isotropic physical cross-links induced by anisotropically distributed chemical cross-links.

EXPERIMENTAL

PVA was Kurarray 117 purchased from Kurarray Co. whose degree of polymerization was 1700. The PVA was completely saponified and was purified in our laboratory by repeating solubilization in water and reprecipitation in methanol. Eight grams of 10% aqueous solution of the purified PVA was cast in a Petri dish whose diameter was 8.6 cm and was served for repetitive freezing and thawing. The gel was frozen in a freezer for 22 h at −20°C and then was thawed for 2 h at room temperature. The repetition was carried out six times. The gel thus obtained was made by physical cross-links and not by chemical or covalent cross-links and was easily solubilized in water above 80°C. The gel and the cross-links are denoted as the "physical gel" and the "physical cross-links," respectively, in this report.

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 46, 1449–1451 (1992)
 CCC 0021-8995/92/081449-03

The physical gel was served for chemical treatment with glutaraldehyde (GA) in order to introduce covalent cross-links in the network structure by treating the gel in GA aqueous solution. The reaction conditions are the following: Stock solution of 25% GA was purchased from Wako Pure Chemical Industries Ltd. First, the physical gel was immersed in a large amount of 0.01% GA aqueous solution for 24 h at 4°C, then the gel was immersed in 350 mL of GA solution that contains 0.08% GA and hydrochloric acid of 0.01*N* at 30°C for 1 h. Thus, the GA-treated gel is denoted as the "chemical gel" and the cross-links in the gel are denoted as "chemical cross-links."

The above-mentioned chemical treatment with GA was carried out under elongation, i.e., the GA-containing physical gel was chemically cross-linked under applying a strain of 200% in the gel network. The strain was defined as the ratio of the length of elongated gel to that of original gel without strain. After being chemically cross-linked under the elongation, the strain applied to the gel was removed and thoroughly rinsed in water.

RESULTS AND DISCUSSION

Typical results that deduced the discussion below are summarized in Figure 1. The numbers in parentheses refer to the gels in Figure 1 in the following discussion. Original physical gel (1) was treated in two ways: one is following the course from (1) to (6), and the other is from (1) to (6′) as a control without the elongation process that is contained in the former process as (2). The chemical gel prepared under applying strain (3) was isotropic and showed no change in appearance. Under the conditions of GA concentration much higher than that employed in this experiment, the gel shrinks by the chemical cross-linking. The chemical gel (3) had the same size, shape, and texture as that of the isotropic original physical gel (1).

The chemical gel was immersed in boiling water to destroy the physical cross-links. The heat-treated chemical gel is denoted as "melted gel" in this paper. The chemical gel heat-treated in boiling water did not swell isotropically but anisotropically as shown by (4) and (5). The anisotropic swelling behavior

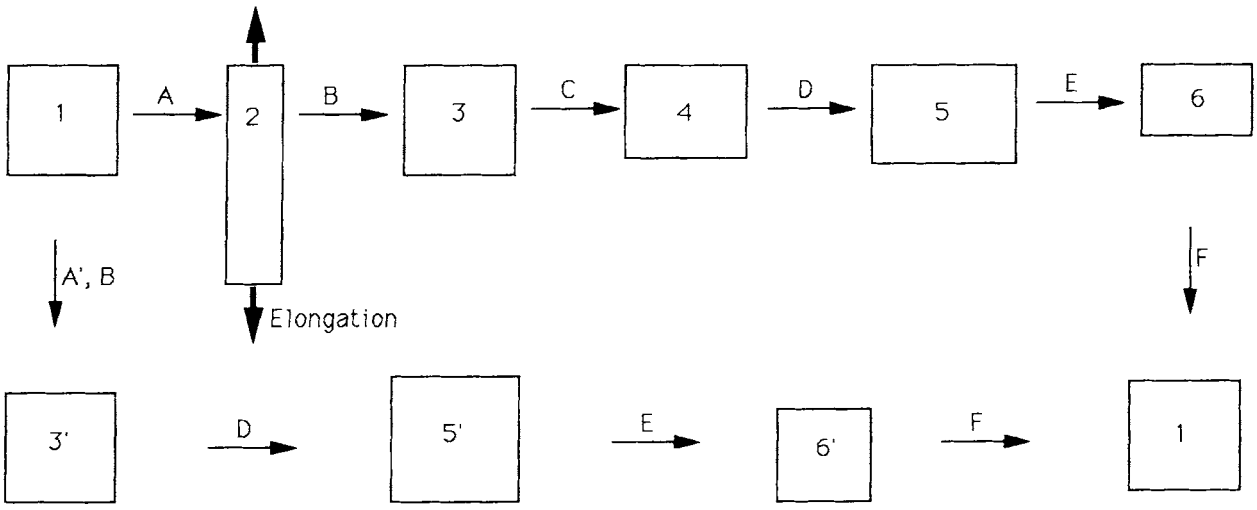

Figure 1 Effect of anisotropically introduced chemical cross-links on the shape restoring of PVA hydrogel. Shape and size of the squares and rectangulars show the relative size measured: (1) original physical gel; (2) under strain of 200%; (3) chemically cross-linked gel (anisotropic chemical gel that is isotropic in appearance at this stage); (4) melted gel (right after melting); (5) melted gel (12 h in water after melting); (6) anisotropic gel deswollen in methanol; (3′) after chemical cross-linking without strain (isotropic chemical gel); (5′) melted isotropic gel (12 h after melting); (6′) isotropic gel deswollen in methanol; (A) chemical treatment with GA under strain of 200%; (B) after removing strain and being thoroughly rinsed in water; (C) right after immersing the gel in boiling water; (D) 12 h immersion in water at ambient temperature, after the heat treatment of 30 s in boiling water; (E) deswelling in methanol for 12 h; (F) reswelling in water for 12 h; (A′) chemical treatment with GA without applying strain or elongation.

depends on the degree of elongation in the chemical treatment, suggesting that the chemical treatment under anisotropic condition resulted in the formation of anisotropic chemical cross-links and that they caused the anisotropic swelling by being removed by isotropic physical cross-links. In other words, the anisotropically introduced chemical cross-links have been depressed by the major presence of the physical cross-links.

The melted gel (5) was deswollen into anisotropic shape (6) in methanol. The anisotropically deswollen gel (6) was immersed in water to swell into isotropic gel (1) whose size and texture was the same as that of the original physical gel. This process shows that the anisotropical melted gel (5) changes into an isotropic physical gel form, suggesting that the anisotropic cross-links can trigger the restoration of the isotropic physical cross-links as in the physical gel. Thus, the anisotropically introduced chemical cross-links were found to trigger the restoration of physical cross-links as in the original gel. This is a novel type of shape memory. The interesting observation shown above can be considered to result from the localization of the physical cross-links and the chemical cross-links in the gel structure. The localization of the chemical cross-links in the chemical treatment has been pointed out by Sakurada and Yoshizaki,[10] but they did not mention that the localization can lead to the function of shape memory as we have shown in this paper. The results shown here suggest that the control of the localization of the chemical cross-links in the gel network is not only possible but also can lead to a novel function of shape memory in the physical gel in much more an enhanced manner than has been expected. Further investigation is under way and will be published elsewhere.

REFERENCES

1. M. Nambu, Eur. Pat. Appl. 820,825 (1982).
2. T. Hirai, Y. Asada, T. Suzuki, S. Hayashi, and M. Nambu, *J. Appl. Polym. Sci.*, **38,** 491 (1989).
3. T. Hirai, K. Hanaoka, T. Suzuki, and S. Hayashi, *Kobunshi Ronbunshu,* **46,** 613 (1989).
4. M. Suzuki, *Koubunnshi Ronbunnshu,* **46,** 603 (1989).
5. T. Shiga and T. Kurauchi, *J. Appl. Polym. Sci.,* **39,** 2305 (1990).
6. M. Nambu, *Kobunshi Ronbunshu,* **47,** 695 (1990).
7. M. Nambu and N. Makino, Eur. Pat. Appl. 870,715 (1987).
8. M. Nambu, *Kino Zairyo,* **7,** 29 (1987).
9. T. Hirai, H. Maruyama, T. Suzuki, and S. Hayashi, *J. Appl. Polym. Sci.,* to appear.
10. I. Sakurada and O. Yoshizaki, *Kobunshi Kagaku,* **10,** 310 (1953).

Received September 3, 1991
Accepted January 1, 1992