Preparation of transparent poly(vinyl alcohol) hydrogel

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ABSTRACT

A transparent hydrated gel is prepared from a poly(vinyl alcohol)(PVA) solution in a mixed solvent consisting of water and dimethyl sulfoxide(DMSO). Upon cooling the PVA solution below the room temperature, a gel is formed as a consequence of crystallization of PVA molecules. Exchange of DMSO in the formed gel with water gives the hydrated PVA gel which is high in tensile strength, water content, and light transmittance.

INTRODUCTION

Hydrogels, defined as the gel which contains water but is not soluble in water, have been widely known for a long time, but it is just recently that they have attracted much attention because of their novel mechanical and biomedical properties. Several research groups have succeeded in preparing hydrogels from PVA (1),(2),(3),(4). All of these gels have high moduli of elasticity and high water contents, but are opaque and translucent or weak. This work is aimed to prepare a PVA hydrogel of high mechanical strengths, high water contents, and excellent transparency.

EXPERIMENTAL

The PVA used is a commercial atactic one and has a viscosity-average degree of polymerization of 1,700 with a degree of saponification of 99.5mol%. DMSO is of chemical grade and used as obtained.

A homogeneous PVA solution with a PVA concentration of 15wt% was obtained by heating the mixture of PVA and a mixed water/DMSO solvent at 140° C for 2 hrs in N₂ atmosphere. The mixing ratio of water to DMSO was kept to 20/80 by weight unless otherwise noted. After lowering the temperature of the PVA solution to 60° C, it was cast on a glass plate and allowed to stand at -20° C for 10 hrs to promote the PVA crystallization. Then the frozen gel was brought into contact with flowing water for 4 days to exchange DMSO in the gel with water. A gas chromatographic analysis exhibited no trace of DMSO in the gel. For comparison, a translucent PVA gel was prepared by freezing an aqueous PVA solution without DMSO at -20° C for 10 hrs, followed by crystallization of PVA at 5° for 10 hrs.

The PVA hydrogel sheets of 1mm thickness prepared by the above procedures were subjected to measurements of tensile

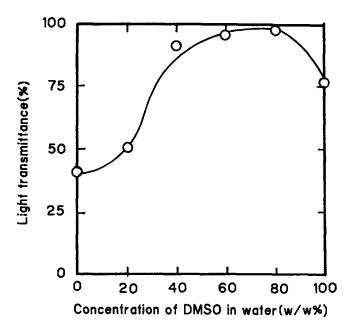


Figure 1, Relation between light transmittanc and concentration of DMSO for PVA hydrogels. (polym.conc.:20g/dl, 570nm, 0.6mm thick).

strength, water content, and visible-light transmittance using the conventional methods.

RESULTS AND DISCUSSION

Figure 1 shows the light transmittance of hydrated PVA gels prepared using mixed solvents of different water/DMSO ratios. As can be seen, transmittance of the gels is higher than 95%, if the water/DMSO ratio of mixed solvent is in the vicinity of 30/70. The tensile strength of new gels became the highest at a water/DMSO ratio of 20/80. The stress-strain curve of the strongest gel is given in Figure 2, together with the curve of the translucent PVA hydrogel. The yield stress for the transparent PVA hydrogel obtained from the mixture with a water/DMSO ratio of 20/80 is much higher than that for the translucent PVA hydrogel prepared from water alone. Moreover, the tensile strength of the transparent PVA hydrogel is approximately 2 times greater than that of the translucent one.

The tensile properties, water content, and visible-light transmittance are summarized in Table 1 for the gel sheets which are 0.6mm in thickness and 85 wt% in water content. It is obvious that the gel prepared from the mixed solvent consisting of water and DMSO exhibits a higher tensile strength, a higher water content, and besides, much more excellent transparency than the translucent gel prepared from the aqueous PVA solution.

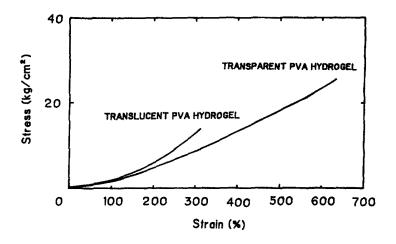


Figure 2. Stress-strain curves of PVA hydrogels.

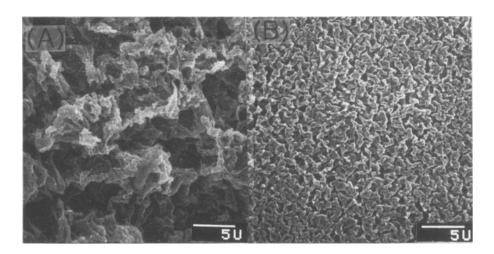


Figure 3. SEM photographs of PVA hydrogel. (A); translusent PVA hydrogel (B); transparent PVA hydrogel

The gel surface was observed by scanning electron microscopy(SEM) after critical-point drying of the hydrated gels using 3-methylbutyl acetate and water. The SEM photographs of the translucent and the transparent PVA hydrogel are shown in Figure 3. As is seen, the surface of the

•	Water content (%)	Light * transmittance (%)	Tensile strength (kg/cm²)	Elongation (%)
W PVA	85	45	13	300
T PVA	85	99	25	650

Table.1 Characteristics of various PVA hydrogels.

W PVA: translucent PVA hydrogel

T PVA; transparent PVA hydrogel

* 570nm, 0.6mm thick

translucent gel has many irregular pores with sizes larger than 3μ m. On the contrary, the surface of the transparent gel prepared from the mixed solvent shows very small regular pores with sizes below 1μ m, distributed densely and homogeneously. The fine pore distribution will account for the high light transparency.

In summary, it is concluded that the low temperature crystallization of atactic PVA in solutions from water and DMSO produces transparent PVA hydrogels with high water contents and excellent mechanical properties. DMSO seems to prevent the PVA solution from freezing which would otherwise lead to phase separation and to prevent the formation of large PVA crystallines. A study is currently underway to learn the mechanism of gelation of PVA in the mixed solvents.

It should be noted that this transparent and highly hydrated gel exhibits a high oxygen permeability and low protein adsorption(5). Therefore, it is expected that this gel will find interesting applications in the biomedical fields where such properties are demanded together with excellent mechanical properties and transparency.

REFERENCES

- 1. M.Watase, K.Nisinari, and Nambu (1982) Polym Comm.24:52
- S.-H.Hyon and Y.Ikada (1983) Report of the poval committee, 83;91
- 3. F.Yokoyama, I.Masada, K.Shimamura, T.Ikawa, and K.Monobe (1986) Colloid Polymer Sci.264:595
- 4. S.-H.Hyon and Y.Ikada (1986) Proceed.Sixth Tihany Symp.6:657
- 5. S.-H.Hyon, W.-I.Cha, Y.Ikada, M.Kita, U.Ogura, and Y.Honda (1988) The Third World Biomaterials Congress, 3:536

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