

Preparation and Properties of Transparent Cellulose Hydrogels

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ABSTRACT: Highly transparent cellulose hydrogels with physical crosslinkage were prepared from nonaqueous organic cellulose solutions and viscose by coagulating and regenerating cellulose in an aqueous solution containing a water-miscible organic solvent. Nonaqueous organic cellulose solutions used were LiCl/dimethylacetamide, paraformaldehyde/dimethyl sulfoxide, and triethylammonium chloride/dimethyl sulfoxide. Preparation conditions and physical properties of the transparent cellulose hydrogels were

studied. The transparency of the cellulose hydrogels depended on the composition of the aqueous solution containing the organic solvent. Furthermore, transparent cellulose hydrogels from viscose showed high tensile strength. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3020–3025, 2003

Key words: cellulose; hydrogels; transparency; swelling; mechanical properties

INTRODUCTION

Polymer hydrogels have been widely utilized as foods, cosmetics, high water-absorbing resins, and so on because of their excellent hydrophilicity. Especially, various transparent polymer hydrogels have been studied as ophthalmic materials such as soft contact lenses.¹ Wichterle and Lim found that a poly(2-hydroxyethyl methacrylate) (HEMA) hydrogel has high transparency and chemical stability, which has been most often used for hydrated soft contact lenses.² Recently, a poly(vinyl alcohol) (PVA) hydrogel has attracted much attention for its potential application to ophthalmic materials. Hyon et al. showed that transparent PVA hydrogel with high water content and tensile strength can be prepared by a low-temperature crystallization technique using a water-dimethyl sulfoxide (DMSO) mixed solvent.^{3,4} On the other hand, to obtain a highly transparent stable cellulose hydrogel, Morita and Nishiyama have proposed chemical crosslinking of regenerated cellulose hydrogel from a cellulose cuprammonium solution.⁵ Ono et al. tried to prepare the cellulose hydrogels by using aggregation and association of cellulose micro-particles by hydrogen bonding.⁶ However, very few reports on physically crosslinked cellulose hydrogels with excellent transparency and mechanical strength are currently available in the literature.

In this study, we show that a new transparent cellulose hydrogel can be prepared by coagulation and regeneration of cellulose from various cellulose solutions with a water-miscible organic solvent (coagulation/regeneration bath) through physical crosslinking, that is, hydrogen bonding. Cellulose solutions used were LiCl/dimethylacetamide (DMAc), paraformaldehyde (PF)/DMSO, triethylammonium chloride (TEAC)/DMSO, and viscose. We investigated the preparation conditions for the transparent cellulose hydrogels, and determined their physical properties such as transparency and tensile strength.

EXPERIMENTAL

Cellulose solutions

Cellulose solutions used in this study were classified into two groups, a nonaqueous organic solution and an aqueous one. As nonaqueous organic cellulose solution, three types of solutions—that is, LiCl/DMAc, PF/DMSO, and TEAC/DMSO, were used. A conventional viscose for rayon and cellophane production was studied as an aqueous case.

Cellulose sources used in this study were a cellulose powder (CF11, Whatman, UK) and a dissolving pulp whose origin was softwood (N-DP). The reason that different cellulose sources were used is follows: CF11 did not dissolve in PF/DMSO and TEAC/DMSO probably because of its high crystallinity, while N-DP caused gelation after dissolution into LiCl/DMAc probably because of a high degree of polymerization.

The cellulose/LiCl/DMAc solution was prepared according to the following procedure described by

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Turbak et al.⁷: CF11 was dehydrated by solvent replacement with DMAc. The mixture of the dehydrated CF11 and fresh DMAc was heated to 150°C for 10 min with stirring. After cooling to 90°C, LiCl was added, and then the cellulose dissolved during cooling to room temperature. The solution obtained was filtered through a G3 glass filter. The solution had 7.0 wt % cellulose concentration in LiCl/DMAc (1:9).

The cellulose/PF/DMSO solution was prepared as follows⁸: The mixture of the N-DP dried at 105°C for 12 h, PF, and DMSO was heated slowly to 120°C, and stirred for 1 h at that temperature. The resultant cellulose solution was filtered through a 250-mesh stainless steel screen to give a solution with a 4 wt % cellulose concentration in PF/DMSO (1: 15).

Cellulose was dissolved in TEAC/DMSO by using the procedure proposed by Kamata et al.⁹: TEAC anhydride was dissolved in DMSO under stirring and heating, and then the dried N-DP was added under heating at 90°C. Then the cellulose solution obtained was filtered through a 250-mesh stainless steel screen to give a solution with a 4 wt % cellulose concentration in TEAC/DMSO (7: 13).

As an aqueous cellulose solution, a technical viscose for cellophane production (cellulose concentration, 9.5 wt %; NaOH, 6.0 wt %) manufactured by Rengo (Japan) was used.

Preparation of cellulose hydrogels

Cellulose hydrogels were prepared by the following procedures: The cellulose solution was cast on a glass plate by using an applicator for thin-layer chromatography plates. The thickness of a cast layer was 0.5 mm for nonaqueous organic cellulose solutions and 1.0 mm for viscose. Immediately, the cast solution was coagulated and regenerated in an aqueous solution containing a water-miscible organic solvent. As a water-miscible organic solvent, acetone, methanol, ethanol, 1-propanol, acetonitrile, tetrahydrofuran (THF), and DMSO were used in this study. Finally, the cellulose hydrogels obtained were washed thoroughly with running water. In the case of viscose, HCl was added to the coagulation/regeneration bath at a total concentration of 0.02–2.0 mol/L for decomposition of cellulose xanthate into cellulose. Furthermore, the cellulose hydrogels from viscose were desulfurized with 0.3 wt % Na₂S at 75°C for 30 min, and bleached with 0.3 wt % NaOCl at room temperature for 15 min before water washing.

Physical properties

The thickness of the swollen cellulose hydrogels was measured by a thickness gauge (SD-25, Kobunshi Keiki, Japan).

In order to measure the water content, the hydrogels were dried in a drying oven at 105 °C until a constant weight was reached. The water content of the hydrogels was calculated from the following equation:

$$\text{water content (\%)} = \frac{(\text{weight of hydrated gel}) - (\text{weight of dried gel})}{(\text{weight of hydrated gel})} \times 100$$

The transmittance of the cellulose hydrogels was measured by the method reported by Hyon et al.⁴ with an ultraviolet-visible spectrophotometer (UV-2200, Shimadzu, Japan) at 550 nm in water at 25°C. The transparency (%) was obtained by converting the transmittance of visible light to the value per 1.0 mm thickness.

The tensile strength of the cellulose hydrogels was measured by a universal-testing machine (Autograph AGS-100G, Shimadzu, Japan). The hydrogel samples were cut to dumbbell test pieces by using a sample punch in accordance with the Japanese Industrial Standards (JIS) K 7113 specification. Measurements were performed at a tensile speed of 50.0 mm/min at 20°C.

Electron microscopic observation

For scanning electron microscopic (SEM) observation, the hydrogels were dried by the *t*-butyl alcohol freeze-drying method¹⁰: The hydrogels were first dehydrated by ethanol, and then the solvent was replaced with 2-methyl-2-propanol, followed by freeze-drying. The dried gels were in turn broken into pieces after refrigeration in liquid nitrogen, and sputtered and coated with Pd–Pt under reduced pressure by an ion sputter (E102, Hitachi, Japan). The cross sections of the cellulose hydrogels were observed using a scanning electron microscope (S-2460N, Hitachi, Japan).

RESULTS AND DISCUSSION

Cellulose hydrogels from a nonaqueous organic solvent system

Figure 1 shows the effect of acetone concentration in the coagulation/regeneration bath on transparency, thickness, water content, and tensile strength of the cellulose hydrogels prepared from the cellulose/LiCl/DMAc solution. The thickness and water content of the hydrogels decreased monotonically. Accordingly, the density of the hydrogels increased and then the tensile strength increased with acetone concentration. On the other hand, the transparency of the hydrogels

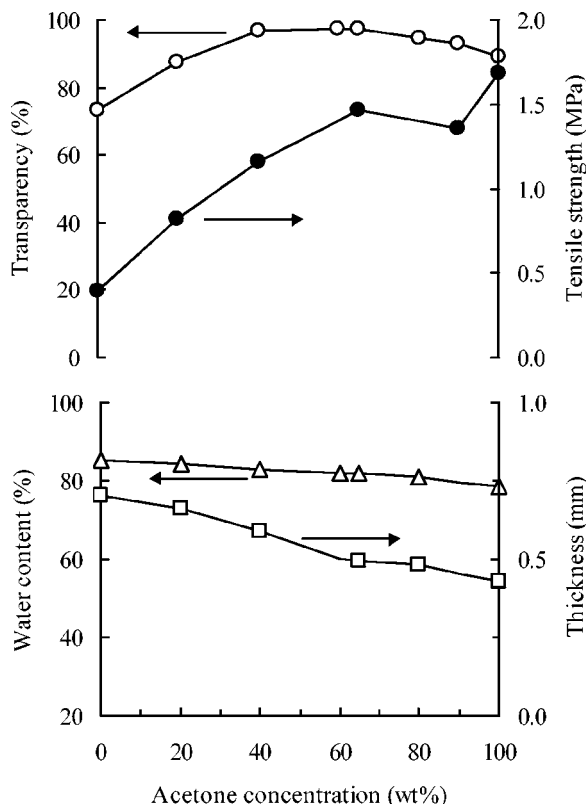


Figure 1 Effect of the acetone concentration of an acetone aqueous solution on the physical properties of the cellulose hydrogels prepared from cellulose/LiCl/DMAc solution. (○) Transparency, (●) tensile strength, (△) water content, and (□) thickness.

increased initially up to 97% around 60 wt % acetone and then decreased gradually.

Figure 2(a) and (b) show the effect of acetone concentration on transparency and thickness of the cellulose hydrogels from the cellulose/PF/DMSO and cellulose/TEAC/DMSO solutions, respectively. Although those behaviors were similar to the cellulose/LiCl/DMAc solution, the maximum transparency and the acetone concentration varied with the types of cellulose solution: LiCl/DMAc (97% at 60 wt %) > TEAC/DMSO (72% at 60 wt %) > PF/DMSO (70% at 80 wt %). The cellulose purity of the cellulose source (CF11: LiCl/DMAc, N-DP: PF/DMSO, and TEAC/DMSO) may contribute to the difference in transparency of those hydrogels.

On the other hand, it is noteworthy that the maximum transparency was obtained in any cellulose solution when the thickness approximately coincided with that of the casting solution (0.5 mm thickness). At just that time, the swelling by water in the coagulation/regeneration bath was balanced with shrinkage by acetone, and consequently, the cellulose hydrogels may have a “specific structure” that makes them transparent.

Table I summarizes the properties of the cellulose hydrogels from cellulose/LiCl/DMAc solution by co-

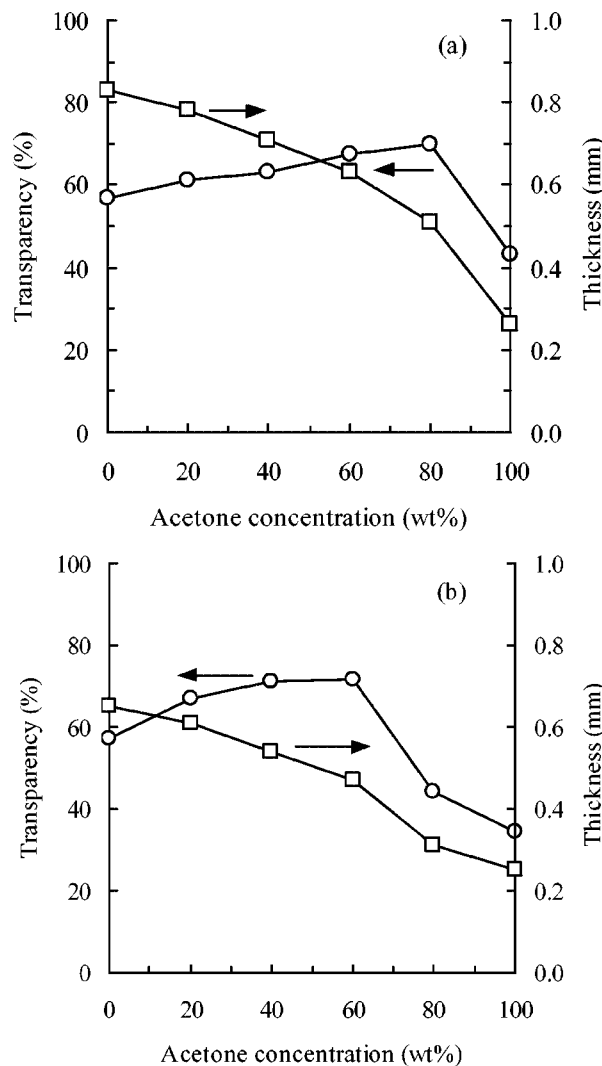


Figure 2 Effect of the acetone concentration of an acetone aqueous solution on the transparency and thickness of the cellulose hydrogels prepared from (a) cellulose/PF/DMSO and (b) cellulose/TEAC/DMSO solutions. (○) Transparency and (□) thickness.

agulation and regeneration with aqueous solutions containing 60 wt % various water-miscible organic solvents. Any organic solvent, especially acetone,

TABLE I
Influence of Water-Miscible Organic Solvents at [organic solvent] = 60 wt % to the Physical Properties of the Cellulose Hydrogels from Cellulose/LiCl/DMAc Solution

Organic solvent	Thickness (mm)	Transparency (%)	Tensile strength (MPa)
Acetone	0.50	97.1	1.43
Methanol	0.53	96.3	1.14
Ethanol	0.52	97.1	1.26
1-Propanol	0.55	95.9	0.87
Acetonitrile	0.48	96.2	0.99
THF	0.60	95.5	0.84
DMSO	0.70	93.8	0.63

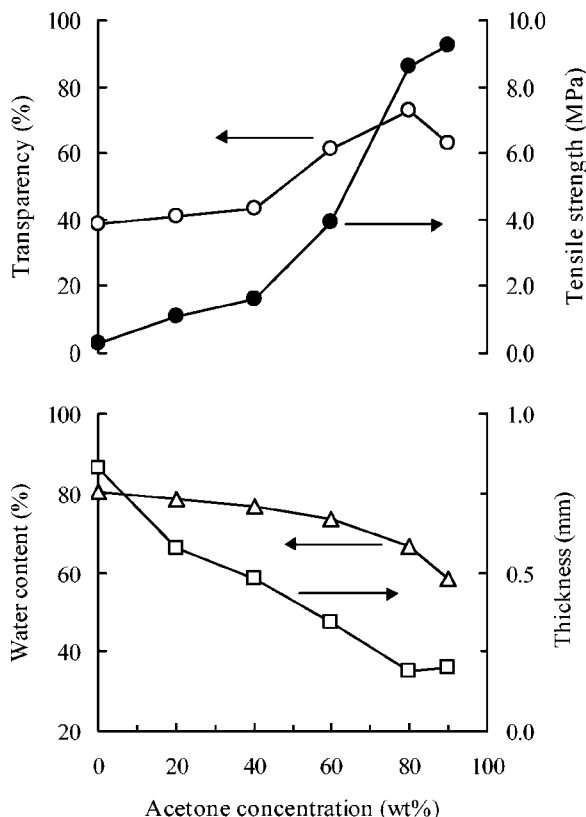


Figure 3 Effect of the acetone concentration in the coagulation/regeneration bath containing 0.5 mol/L HCl on transparency, thickness, water content, and tensile strength of the cellulose hydrogels prepared from viscose. (○) Transparency, (●) tensile strength, (△) water content, and (□) thickness.

methanol, and ethanol, gave highly transparent cellulose hydrogels with over 90% of transparency.

Moreover, highly transparent hydrogels tend to have high tensile strength as transparent PVA hydrogel.³ Since highly transparent hydrogels have small thickness and also the mechanical strength of a heterogeneous material with many defects is generally small, the inner structures of such hydrogels may be relatively dense and homogeneous.

Cellulose hydrogels from viscose

Further, we attempted to prepare transparent cellulose hydrogels from viscose as an aqueous cellulose solution. Since viscose is an alkali solution of cellulose xanthate, hydrochloric acid was added to the coagulation/regeneration bath for decomposition of cellulose xanthate into cellulose.

Figure 3 shows the effect of the acetone concentration in the coagulation/regeneration bath containing 0.5 mol/L HCl on transparency, thickness, water content, and tensile strength of the cellulose hydrogels prepared from viscose. Their behavior was similar to those of the nonaqueous organic cellulose solutions.

That is, the transparency of the cellulose hydrogels from viscose initially increased up to over 70% at 80 wt % acetone, and then decreased. The thickness of the hydrogels decreased from 0.8 to 0.2 mm as acetone concentration increased. However, the maximum transparency of the hydrogels from viscose was lower than that of the hydrogels from nonaqueous organic cellulose solutions, and the thickness was fairly small for its casting thickness. Although such differences may be attributed to a different dissolution state of cellulose (cellulose xanthate in viscose), the detail is not clear. On the other hand, the tensile strength of the transparent hydrogels from viscose increased remarkably in the high concentration region, probably because of the high density of the hydrogels due to the low water content.

The influence of HCl concentration in the coagulation/regeneration bath ([acetone] = 80 wt %) on the properties of the cellulose hydrogels prepared from viscose is indicated in Figure 4. While viscose could not coagulate when acid concentration was less than 0.02 mol/L, the transparency and tensile strength of the hydrogels increased as HCl concentration decreased. When the HCl concentration was 0.1 mol/L, each value reached 88% and 13.7 MPa. In particular, the tensile strength corresponds to 10 times of those of

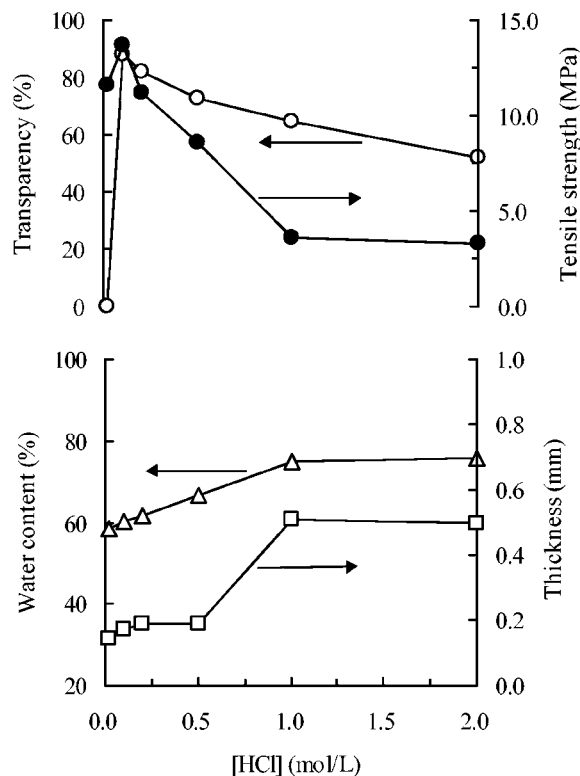


Figure 4 Effect of the HCl concentration in the coagulation/regeneration bath ([acetone] = 80 wt %) on the physical properties of the cellulose hydrogels prepared from viscose. (○) Transparency, (●) tensile strength, (△) water content, and (□) thickness.

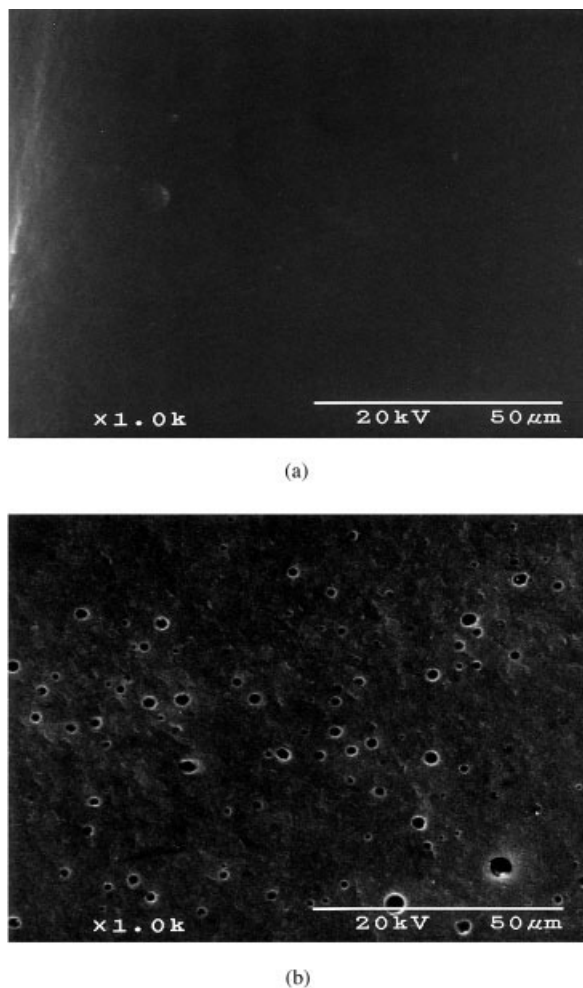


Figure 5 SEM micrographs of the cross section of the cellulose hydrogels from viscose. (a) Transparent hydrogel prepared by coagulation and regeneration with an aqueous solution containing 0.5 mol/L HCl and 60 wt % acetone, and (b) translucent hydrogel prepared by coagulation and regeneration with 0.5 mol/L HCl solution without acetone.

the hydrogels from nonaqueous organic cellulose solutions. However, it took a very long time to coagulate and regenerate viscose at low HCl concentrations.

On the contrary, the thickness increased with HCl concentration. At high HCl concentration, a skin layer tended to be formed immediately after contact between viscose and the coagulation/regeneration bath, and then the coagulating and regenerating solution diffused slowly into the inside of the cast cellulose solution through the skin layer. Accordingly, the hydrogels could not shrink as much, and the inner structure of the hydrogels could become heterogeneous, as indicated by the low tensile strength.

Figure 5 displays the SEM photographs of the cross section of the transparent hydrogel from viscose (a) and the translucent one (b). The transparent hydrogel was prepared by coagulation and regeneration of viscose with an aqueous solution containing 0.5 mol/L

HCl and 60 wt % acetone, while the translucent hydrogel was prepared in 0.5 mol/L HCl solution without acetone. As is seen, many pores with a diameter of ca. 2 μm were observed in the translucent hydrogel (b), though cross section of the transparent one was extremely smooth and also the transparent PVA hydrogel had a homogeneous network structure.³ Air bubbles arising from the gas such as H_2S evolved during coagulation and regeneration may be trapped as these pores inside the hydrogel.

In general, transparency of materials is governed by reflection, absorption, and scattering.¹¹ Since shape and molecular structure of the hydrogels are same between the transparent hydrogels and the translucent ones, influences of reflection and absorption may be small in this study. When a difference in transparency can be attributed only to scattering of the light from certain objects or domains (scatterers) in the system, the transparency may be affected by the distribution of the refractive index. In other words, there are three main factors, which are (1) difference, that is fluctuation, between the refractive index of a scatterer and the average one in the system, (2) the size of the scatterer, and (3) the volume fraction of the scatterers.

In the case of the hydrogels from viscose, it is thought that a fluctuation of the refractive index by the difference of the density of the voids and bulk phase causes scattering, and consequently makes the hydrogel hazy. As mentioned above, hydrogels coagulated slowly at low HCl concentrations tend to be transparent and have high tensile strength. This fact suggested that the air bubbles were released from the cellulose hydrogels by the completion of coagulation and consequently the voids disappeared.

However, the slight difference in transparency between the cellulose hydrogels from the nonaqueous organic cellulose solution cannot be explained by pores, since there are no pores in that hydrogel. Therefore, significantly smaller scatterers than pores may contribute to the scattering in this case. Although we tried microstructure analysis of the cellulose hydrogels by a light scattering study, all our attempts were unsuccessful because of weak scattering intensity from the hydrogels. Ando and Konishi studied the microstructure of the cellulose hydrogel prepared from viscose by a small-angle x-ray scattering and an ultras-small angle x-ray scattering methods.¹² Accordingly, they found out the structural difference between the transparent hydrogels and the translucent ones in studies—that is, the translucent hydrogel has the structures of larger dimension than a micron in the system, and has a smaller average diameter (80 \AA) of the high-density region including crystallite than that of the transparent one (120 \AA). However, what is the above-mentioned “specific structure” that makes the cellulose hydrogels transparent has not become apparent yet.

In the case of the translucent hydrogels from viscose with large pores observed by SEM, the lower transparency was due mainly to the large fluctuation. On the other hand, in the case when no obvious structure such as pores, particles, or aggregates was observed, there were very few scatterers with large fluctuations. Accordingly, "specific structure" of highly transparent hydrogels may be the structure whose contrasts between larger domains is small, that is, has a small distribution of density.

CONCLUSIONS

Highly transparent cellulose hydrogels with physical crosslinkage were prepared from three nonaqueous organic cellulose solutions and viscose by coagulating and regenerating cellulose in an aqueous solution of a water-miscible organic solvent. Physical properties of the hydrogels were mainly dependent upon the composition of the coagulation/regeneration bath, and the maximum transparency of the hydrogel was 97% in the case of a nonaqueous organic solution. Moreover, the transparent hydrogel from viscose had an extremely high tensile strength (13.7 MPa), though the maximum transparency (88%) was slightly lower than that of the hydrogels from an organic cellulose solution.

In the case of the nonaqueous organic cellulose solutions, the highly transparent hydrogels were obtained when swelling by water was balanced with shrinkage by the organic solvent. However, in the case of viscose, the transparency of hydrogels with smaller

thickness is higher, which may be attributed the dissolution states of the cellulose.

In this study, scattering of the light might greatly affect the transparency of the cellulose hydrogels. Highly transparent hydrogels may have the structure that contrast between larger domains is small.

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References

1. Osada, Y.; Gong, J. P.; Tanaka, Y. In *Functional Monomers and Polymers*, 2nd ed.; Takemoto, K., Ottenbrite, R. M., Kamachi, M., Eds.; Marcel Dekker: New York, 1997; Chap 14.
2. Wichterle, O.; Lim, D. *Nature* 1960, 185, 117–118.
3. Hyon, S. H.; Cha, W. I.; Ikada, Y. *Polym Bull* 1989, 22, 119–122.
4. Hyon, S. H.; Cha, W. I.; Ikada, Y. *J. Biomater Sci, Polym Edn* 1994, 5(5), 397–406.
5. Morita, T.; Nishiyama, T. *Jpn Pat* 05-237,142, 05-239,263, 1993.
6. Ono, H.; Shimaya, Y.; Kanekiyo, K.; Yamane, C. *Preprints of '99 Cellulose R&D 6th Annual Meeting of the Cellulose Society of Japan*, 27, 1999 (in Japanese).
7. Turbak, A. F.; Kafrawy, A. E.; Snyder, F. W.; Auerbach, A. B. *U.S. Pat.* 4,302,252, 1981.
8. Hammer, R. B.; O'Shaughnessy, M. E.; Strauch, E. R.; Turbak, A. F. *J Appl Polym Sci* 1979, 23, 485–494.
9. Kamata, M.; Tabushi, I.; Asaeda, T.; Morimoto, S.; Aoki, Y. *Jpn. Pat.* 60-144,332, 1985.
10. Inoue, T.; Osatake, H. *Arch Histol Cytol* 1988, 51(1), 53–59.
11. The Chemical Society of Japan, Ed. *Kikan Kagaku Sosetsu No. 39—Refractive Index Control of Transparent High Polymers*; Japan Scientific Societies Press: Tokyo, 1998; Chap 1 (in Japanese).
12. Ando, H.; Konishi, T. *Phys Rev E* 2000, 62(1), 727–733.