

## Rapid Swelling of Thermosensitive Gel Immobilized with Cellulose Powder

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Cellulose powder was immobilized in a microporous poly(*N*-isopropylacrylamide), PNIPA, gel to control the swelling and shrinking rates of the gel. The fast response gel, of which rates on shrinking and swelling are higher than the conventional gel, was prepared from the PNIPA gel with a treatment of the freeze-drying and water hydration. Microporous structure formed by the freezing treatment was effective to increase the shrinking rates irrespective of cellulose contents. On the contrary, the swelling rates were strongly dependent on the cellulose contents; microporous gels with and without 6 wt% cellulose respectively were reached to be equilibrium at 14 and 130 min as the shrunken gels at 40°C were immersed in water at 22°C.

Key words: thermosensitive gel, microporous structure, freeze-drying, swelling kinetics, cellulose

### 1. INTRODUCTION

Response rates of stimuli-responsive gels are one of the important factors for the success of most applications of these gels. The porous structure of stimuli-responsive gels has been shown to cause an increase of the volume change rates of gels; a variety of protocols have been developed such as  $\gamma$ -irradiation of poly(vinyl methyl ether) solution to gelate [1], comb-type polymer networks [2], a temperature-induced phase separation [3,4], etc [5,6]. Among these protocols, we have reported that treatments of the freeze-drying (FD) and water hydration or those of freezing and subsequent thawing were effective to form the porous structure (5-30  $\mu\text{m}$ ) on thermosensitive gels [7]. The FD-treated poly(*N*-isopropylacrylamide) gel, abbreviated as PNIPA gel hereafter, shrinks approximately  $10^1$ - $10^3$  times faster than an untreated gel (conventional gel). However, the swelling rate was independent on the porous structure formed by freezing. SEM microphotographs for the cross-section of the FD-treated gel at shrinking state indicated that the pores disappeared after shrinking, and then the FD-treated gel acted as a nonporous gel. Some of the protocols for the preparation of fast shrinkable gel are effective to enhance only shrinking rates of thermosensitive gels [2, 6, 7, 8]. To construct the stimuli-responsive gel devices, the control of the swelling rate is also important.

Cellulose powder was selected to immobilize in the PNIPA gel as the typical hydrophilic-polymer, which was used as an absorbent material of water. The principal hypothesis employed here is that the pore size, microstructure, or other properties of microporous gel should be affected when the PNIPA gel containing hydrophilic polymer is frozen. Thus, effects of cellulose immobilization on the swelling kinetics of the FD-treated PNIPA gels were investigated to make the gel swelling fast.

The purpose of this research is to make swelling and shrinking rates of PNIPA gel fast using the freeze-drying treatment. Swelling and shrinking properties induced by temperature change, an effective porosity of gels, and viscoelasticity of gels were studied to clarify the effects

of cellulose immobilization on the pore formation during the freezing process.

### 2. EXPERIMENTAL

#### 2.1 Materials

PNIPA was purchased from Wako Pure Chemical. Cellulose powder (20-100 $\mu\text{m}$ ) was purchased as the column chromatography grade from Merck. All other chemicals were of guaranteed grade or the best commercially available.

#### 2.2 Polymerization of PNIPA gel immobilized with cellulose powder

The cylindrical PNIPA gel crosslinked by 5 mol% of *N,N'*-methylenebisacrylamide was prepared in silicone tubes ( $\phi$  2mm in diameter) in the same way as described in our previous paper [7]. Cellulose powder (0-10 wt%) was suspended in the monomer solution. The DC motor serves to spin the tubes filled with the pre-gel solution horizontally (with the cylinder parallel to the ground) to keep the cellulose powder in suspension as gelation occurred. The cellulose content (wt%) in gels was defined as the ratio against the total weight of gel just after polymerization. After washing, some conventional gels were frozen at -20°C and then freeze-dried. The gels were re-swollen in water at 22°C. The water content of the gel at 22°C was determined by weighing the gel before and after drying. An effective porosity of gels as the fraction of total gel volume occupied by interconnected pores (void spaces) through which water can flow was determined by the procedure described in the previous paper [4]. From the mass lost by the sample under a known applied mechanical pressure, the effective porosity was determined at 22°C.

#### 2.3 Measurements for swelling

Change of the gel length ( $L$ ) was determined with time by pictures recorded on video-tape, when the temperature was jumped from 40 to 22°C.  $(L-L_0)/(L_\infty-L_0)$  was calculated as the swelling degree, where  $L_0$  and  $L_\infty$  are the gel length at 40°C and at

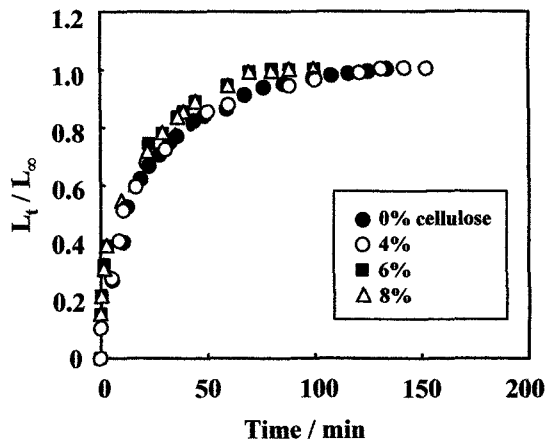


Fig. 1 Swelling profiles of the conventional PNIPA gels immobilized cellulose. The gels equilibrated at 40°C were cooled to 22°C for swelling.

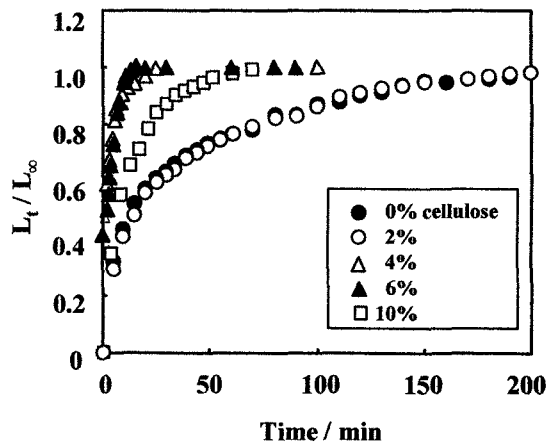


Fig. 2 Swelling profiles of the microporous FD-treated gels immobilized cellulose. The gels equilibrated at 40°C were cooled to 22°C for swelling.

equilibrium of 22°C, respectively. Swelling time is defined as the time taken to reach 98% fractional uptake of water [9].

#### 2.4 Reappearance of shrinking/swelling process

The PNIPA gel rod immobilized with 6 wt% cellulose was freeze-dried and re-hydrated in water at 22°C. The equilibrated gel rod was cut into 60 mm ( $L_i$ ). Then the temperature of the gel rod was jumped to 40°C. After the shrinking of three min, the gel rod was transferred to the water bath at 22°C. It was allowed to swell until the length of the gel rod reached 60 mm. This procedure was repeated twice.

#### 2.5 SEM

The swollen conventional gels at 22°C with and without 6 wt% cellulose were freeze-dried. The cross-sectional morphology of gels were observed by SEM (Hitachi S-4500).

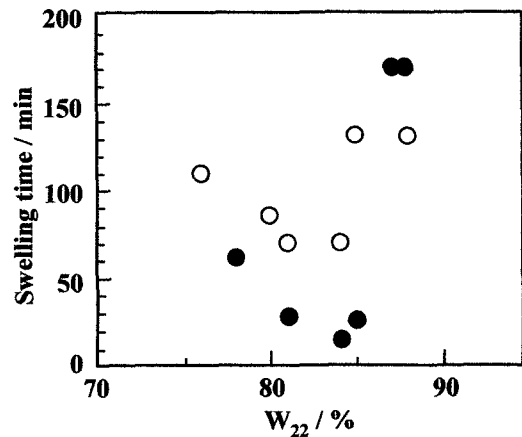


Fig. 3 Water content dependence of the swelling time for the cellulose immobilized gels. The cellulose powder was immobilized on the conventional (O) and the FD-treated (●)gels.

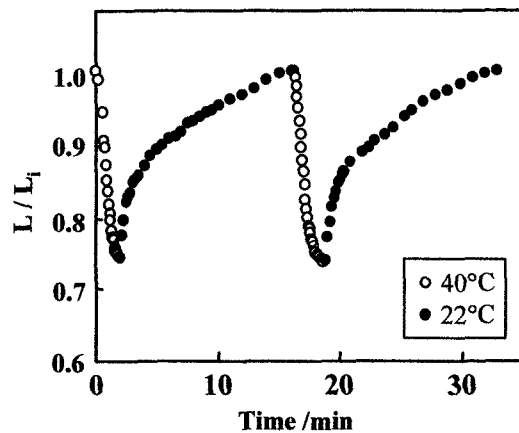


Fig. 4 Reappearance of shrinking and swelling control of the FD-treated gels with 6 wt% cellulose. The gels were heated to 40°C for shrinking and cooled to 22°C for swelling.

#### 2.6 Dynamic mechanical measurements

The slab-shaped gels were prepared for the dynamic mechanical measurements (TMA-SS6100, Seiko Instrument Co.). A synthesized wave strain (0.1 Hz) was loaded on the gel at 22 and 50°C in water. The compressive modulus,  $E^* = E' + iE''$ , was obtained, where  $E'$  and  $E''$  are the storage and loss moduli, respectively. The strain was kept within 1% of the gel thickness.

### 3. RESULTS AND DISCUSSION

#### 3.1 Effects of cellulose immobilization on swelling kinetics

Swelling profiles of the conventional gels containing 0-8 wt% cellulose were shown in Fig. 1. These profiles indicated that cellulose immobilization has only a little effect on the swelling kinetics of conventional PNIPA

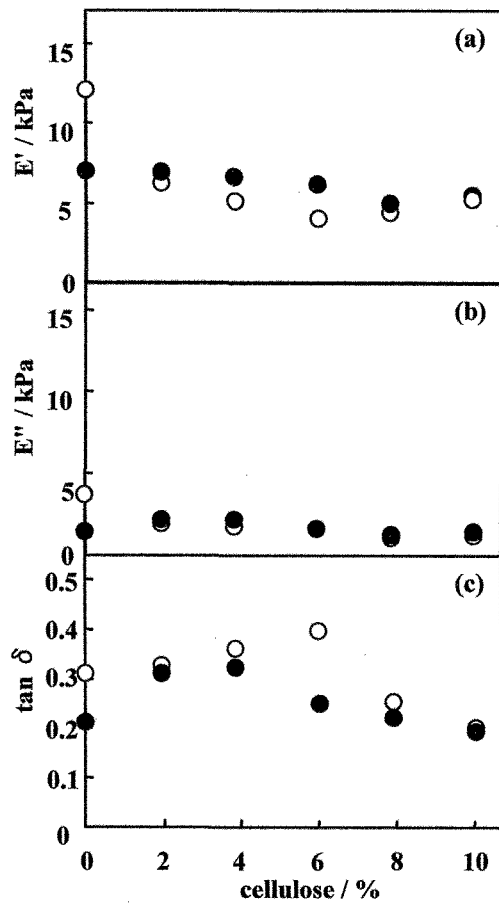


Fig. 5 Relationship between  $E'$ ,  $E''$ , or  $\tan \delta$  and the cellulose content.  $E'$  (storage modulus) and  $E''$  (loss modulus) were determined under 0.1 Hz of synthesized wave strain at 22 (●) and 50°C (○).

gels. On the contrary, the swelling time could be drastically shortened for the FD-treated gels (Fig. 2). In the case of the PNIPA gel containing 6 wt% cellulose, the swelling time for the gels with and without the FD-treatment are 14 and 170 min, respectively. Accordingly, dependence of cellulose contents on the swelling time was studied using the conventional and the FD-treated gels. Water content of the gel at 22°C defined as  $W_{22}$  was plotted against the swelling time of gels (Fig. 3). Figure 3 shows each curve gave a minimum at around 6 wt% cellulose (around 83-84 % of  $W_{22}$ ).

In the previous paper [7], we reported the FD-treatment brings the porous structure on the PNIPA gel and this porous structure is primarily responsible for the fast-response during the shrinking process. The shrinking of the PNIPA gels can be accelerated in the same way irrespective of cellulose contents (data not shown). These cellulose immobilized PNIPA gel rods were reached to be equilibrium within 3 min as the temperature changed from 22 to 40°C. Since it took approximately 100-120 min to be equilibrium for the shrinking process of the conventional gel, the FD-treated PNIPA gel containing 6 wt% cellulose can shrink and swell much faster than the conventional gel before the

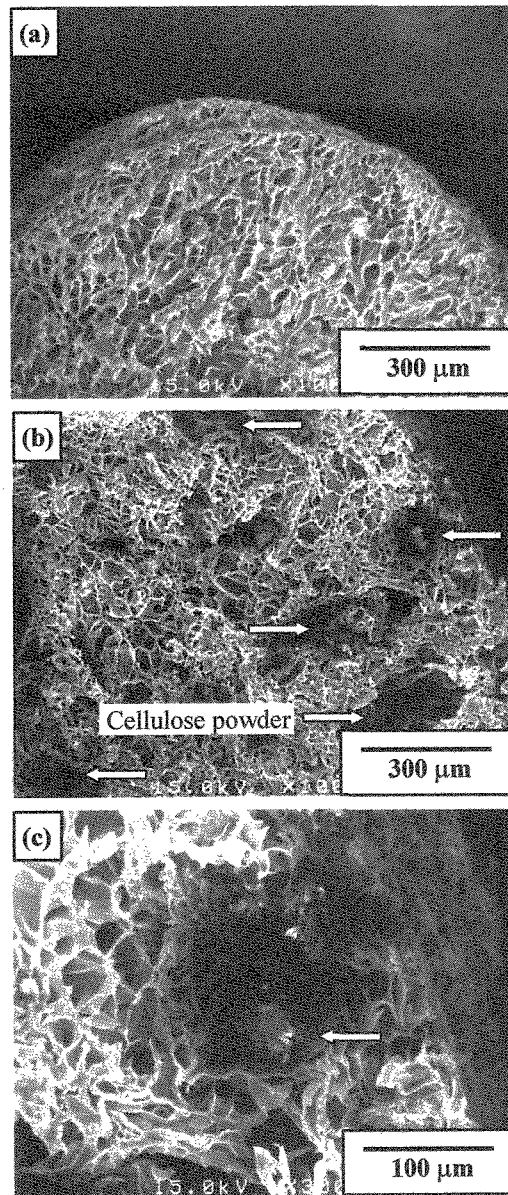


Fig.6 SEM microphotographs of PNIPA gels. (a) The freeze-dried gel prepared from the swollen conventional gel without cellulose. (b) (c) The freeze-dried gel prepared from the swollen conventional gel with 6 wt% cellulose.

FD-treatment.

When the gel became porous, some of the struts are considered to lock into position because of hydrophobic interaction or polymer entanglement. The formed interaction between polymer chains during freezing process is considered to obstruct the diffusion of polymer networks. Therefore, swelling time of the gel rod without cellulose was increased from 130 to 170 min by freeze-drying.

Reappearance of the shrinking-swelling cycle was investigated using the FD-treated gel containing 6 wt% cellulose. As shown in Fig. 4, the fast shrinking-swelling cycle can be repeated. This means the microporous

structure formed by the FD-treatment is stable and this fast response gel can be applied to the recyclable device.

### 3.2 Microstructure of polymer networks

Gehrke and coworkers described importance of the gel microstructure for the shrinking/swelling kinetics of thermosensitive hydrogels [4,10]. The volume change rates of microporous gels are strongly affected by the interconnectivity of micropores (closed cell or open cell). Swelling and shrinking in a microporous gel with interconnected pores involves two different mass transfer steps: diffusion in the pore wall (the polymer strut) and convection through the pores. In general, the gel swelling is explained as the mutual diffusion process between the polymer and the solvent. Therefore, swelling time for the conventional gel is determined by the gel size. On the contrary, the characteristic diffusional path length of microporous gel is not the gel length but half the thickness of the strut because water is expelled through the interconnected pores. Thus, the microporous gels with interconnected pores can transport water very fast. In the case of the gel with unconnected pores or the non-porous conventional gel, the volume change remains relatively slow.

To evaluate the interconnectivity of pores in the FD-treated gels, the effective porosity was measured as the void volume of gels. Both of the effective porosities for the conventional and the FD-treated gels were obtained as less than 0.12 irrespective of cellulose amounts inside gels. These results mean that the almost all micropores are closed and cellulose immobilization does not affect the interconnectivity of micropores. The possible explanation is that the pores are connected at the early stage of shrinking process by the polymer aggregation due to the hydrophobic interaction. Then water can be expelled through the interconnected channels with a convective flow.

Viscoelasticity of gels was studied to clarify the effect of cellulose immobilization on the polymer network. Figure 5 shows dependency of cellulose contents on  $E'$ ,  $E''$ , and  $\tan\delta$  ( $= E''/E'$ ). Although  $E'$  and  $E''$  at the swelling state of gels were not dependent on cellulose contents, the cellulose contents could control  $E'$  at the shrinking state (50°C). Decrease of  $E'$  corresponds to the increasing heterogeneity of polymer networks. Increase of  $\tan\delta$  at around 4-6wt% means the gel became viscoelastic.

Actual volume change of gels becomes smaller when the cellulose is immobilized within the PNIPA gel; equilibrated values of  $L/L_i$  at 40°C for 0, 6, and 10wt% cellulose respectively were 0.20, 0.30, and 0.44, where  $L_i$  is the initial gel length at 22°C. Consequently, the swelling time decreases with the increment of the cellulose content. On the contrary, the cellulose powder excessively added probably obstruct network motion during the swelling process.

### 3.3 Morphology of microporous PNIPA gels containing cellulose

SEM microphotographs of the FD-treated gels with and without 6 wt% cellulose were shown in Fig. 6. Honeycombed pores generated by freeze-drying are observed at the cross-section of the cylindrical gels. Figure 6a shows that the gel morphology did not alter

for the direction of depth. Figures 6b and 6c show the microstructure of the FD-treated gels containing 6 wt% cellulose; Arrows in the figure designated the cellulose powder entrapped inside gels. These pictures clearly indicated that cellulose powder generated the caves or open spaces of approximately 50-200 $\mu$ m in diameter within gels.

The polymer chains are probably gathered and condensed as the water inside gel froze. After sublimation of the ice, the porous structure remained. It is considered that the cellulose powder is entrapped in the polymer strut or walls constructed pores. The open space surrounding cellulose particles is supposed to be formed by freeze-drying, when the ice was sublimated. The presence of open space can enlarge the surface area to absorb water into gels, and also work as the partially connected channels. Accordingly, cellulose immobilization can drastically enhance the water uptake due to the convective flow.

## 4. CONCLUSION

Swelling rates of the FD-treated PNIPA gel were accelerated with immobilization of the cellulose powder. During the freeze-drying process, the hydrophilic cellulose can form the large pores, which act as the connected or partially connected channels during the gel swelling. The large pores formed by the FD-treatment can lead a decrease of the diffusional path length at the swelling process and the convection through the channels inside gels.

The microporous PNIPA gel containing 6 wt% cellulose can swell 10 times faster than the conventional gel. The freeze-drying method is effective to control the swelling/shrinking rate of the thermosensitive gels.

## ACKNOWLEDGEMENTS

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