Polymer Bulletin 58, 213–223 (2007)
DOI 10.1007/s00289-006-0618-z

Polymer Bulletin

Dewatering of organic slurries using reinforced thermosensitive porous gels

Effect of preparation conditions on the dewatering performance of a gel

Takehiko Gotoh (✉), Hiroshi Okamoto and Shuji Sakohara

Department of Chemical Engineering, Hiroshima University, Higashi-Hiroshima, 739-8527, Japan
e-mail: tgoto@hiroshima-u.ac.jp

Received: 21 July 2005 / Accepted: 15 September 2005

Summary

The use of a thermosensitive porous gel for dewatering organic slurries was investigated. The gel was synthesized from *N*-isopropylacrylamide (NIPAM), the monomer and *N,N'*-methylenebisacrylamide (MBAA), a crosslinker. A porous gel was produced by simple radical polymerization at higher temperature than the LCST (Lower Critical Solution Temperature) of the *N*-isopropylacrylamide polymer. At such a high temperature, phase separation occurs as polymerization proceeds, and a porous structure is formed. The thermosensitive porous gel, which was supported by stainless steel wire, was prepared and the effect of preparation conditions such as the concentration of crosslinker and monomer used on the dewatering performance of the gel was examined. The effects of these parameters on gel structure and the relationship between gel structure and absorption rates were also examined.

Introduction

Organic slurries that are produced as waste streams from food processing plants frequently contain useful components such as proteins, vitamins and enzymes, which could be further used as materials for drugs or functional foods. However, dewatering of the slurry is necessary to recover such useful materials. Heat drying and mechanical dewatering are well known conventional dewatering methods. Heat drying requires considerable energy, and mechanical dewatering requires some chemicals to aggregate the slurry. Moreover, heat drying is undesirable because most proteins in the organic slurry would be denatured by this treatment. The chemicals required for mechanical dewatering are not easy to separate from the recovered materials. Therefore, these conventional dewatering methods are not adequate for the recovery of useful materials from such organic slurries. Previous studies of applications of thermosensitive gels to dewatering or extraction processes have been reported [1, 2, 3], because such a

---

Presented at 44th P.M.M. Microsymposium "Polymer Gels and Networks", Prague, 10–14 July 2005 process is not energy intensive and requires no chemicals. However, the swelling or water-absorption rate of gels is slow and the mechanical strength of most gels is not high enough to permit their use in a dewatering process. To solve the problem, porous gels have been developed. A porous gel swells much faster than a non-porous gel. Hirasa *et al.* synthesized porous poly(vinyl methyl ether) (PVME) or poly(*N*-isopropylacrylamide) (PNIPAM) gels by the γ-ray irradiation of PVME or PNIPAM, which are thermosensitive polymers [4, 5]. Huang *et al.* investigated the effect of salt solutions on the swelling behavior of a porous gel [6] and the relationships between their swelling pressure and swelling behavior [7]. They proposed a new concept for a dewatering process for activated slurry using a porous PVME gel, and showed that the process is energy-saving compared with conventional mechanical dewatering processes [8]. Furthermore, Akehata *et al.* recently applied this concept to concrete with a spiral feeder type dehydrator [9]. However, the most serious problem in this process in industrial use is the γ-ray irradiation used to synthesize a porous gel. Kabra and Gehrke synthesized fast responsive PNIPAM gels by the copolymerization of NIPAM with a crosslinker at room temperature for 9 min and then continued the polymerization at a temperature above LCST (Lower Critical Solution Temperature) for 24h [10]. Wu *et al.* reported on microporous PNIPAM gels prepared by the radical copolymerization of NIPAM with a crosslinker at a temperature above the LCST in the presence of (hydroxy propyl) cellulose as a pore-forming agent [11]. The authors have described a simple method of synthesizing porous gels by the radical copolymerization of NIPAM or *N,N*-diethylacrylamide with a crosslinker at a constant temperature above the LCST. The gel consisted of small gel particles and pores. The porous structure of the gel was developed by increasing the preparation temperature. The relationships between the preparation temperature and elastic moduli of gels in water at various temperatures and between the heat transfer rate and swelling/shrinking rate have been investigated [12].

The authors reported on a method for preparing a reinforced thermosensitive porous gel, which was supported by a stainless steel net, which improves its mechanical strength and applied the porous gel to the dewatering of organic slurry [13]. A slab gel with the support swelled in one direction i.e., in the thickness direction. In other words, the porous gel could swell anisotropically because of its low elastic modulus. The gel was strong enough to be used more than 50 times for the dewatering of an organic slurry. The water content of the slurry was decreased from 91 to 60 percent and the dewatered cake was easily removed from the gel surface. The relationship between the preparation conditions and the absorption rate of the gel was examined. It was found that an increase in crosslinker concentration led to an increase in absorption rate because of the porous structure that developed with increasing crosslinker concentration. The porous structure could be adjusted by the preparation conditions of the gel and the absorption rate of the gel was influenced by the swelling property of the gel. In spite of this, further study is needed to improve the absorption rate of the gel.

It is well known that the osmotic pressure of a gel, which determines its swelling property, is the sum of four component pressures; rubber elasticity, affinity between polymer and solvent, counter-ion pressure and mixing enthalpy [14, 15]. Rubber elasticity is determined by the polymer concentration in the gel. The affinity of polymer to solvent largely affects the absorption capacity of the gel. The counter-ion pressure plays an important role in the swelling properties of ionic gels. In this paper, the effect of preparation conditions such as the concentration of crosslinker and monomer, which affect rubber elasticity and mixing enthalpy of a gel, on swelling properties were examined. The relationship between preparation conditions and the water-absorption rate of the gel was also examined.

Experimental

Materials

NIPAM used as monomer was obtained from the Kojin Co. Ltd. (Tokyo, Japan). *N,N'*-methylenebisacrylamide (MBAA) was used as a crosslinking agent (crosslinker). *N,N,N',N'*-tetramethylethylenediamine (TEMED) and ammonium peroxodisulfate (APS) were used as a polymerization accelerator and initiator, respectively. They were all reagent grade and were purchased from Kanto Chemicals (Tokyo, Japan). The NIPAM monomer was purified by recrystallizing from hexane.

Table 1. Synthesis of the gel[a].

Gel name	NIPAM ($mol\cdot m^{-3}$)	MBAA ($mol\cdot m^{-3}$)	DMF (wt%)
G1	2000	20.0	0
G2	2000	60.0	0
G3	2000	120.0	0
G4	2000	60.0	10
G5	2250	67.5	10
G6	2500	75.0	10

[a] concentration of TEMED: 10 $mol\cdot m^{-3}$ concentration of APS: 0.5 $mol\cdot m^{-3}$. Synthesis temperature was 50 °C, synthesis time was 3 h.

Preparation of the reinforced gel

The method used to prepare the reinforced porous thermosensitive gel has been reported previously [13]. Table 1 shows the concentrations of the materials used in the synthesis of the gels. The gel was synthesized in a mold, consisting of two glass plates, a 25-mesh stainless steel net and a 5 mm thick acrylic resin spacer. The stainless steel net was made of 0.5 mm diameter wire and was fixed between two glass plates. The mold was purged with nitrogen prior to use and immersed into a water bath at 50 °C, higher than the LCST of the poly(NIPAM). The monomer, the crosslinker and accelerator were dissolved together in an aqueous solution of dimethylformamide (DMF). The porous gels were prepared with 10 wt% DMF aqueous solutions in this experiment to increase the solubility of the NIPAM monomer because the maximum solubility of NIPAM monomer in pure water is 2000 $mol\cdot m^{-3}$. A solution of APS was prepared separately. The solutions were purged with nitrogen gas at 50 °C before the polymerization. These two solutions were mixed and injected immediately into the mold, the reaction was complete within one hour. The gel was left at 50 °C for two additional hours to complete the reaction. The gel, which contained the net was detached from the mold and then washed in distilled water to remove residual chemicals. The dimension of the gel was 6 cm in width, 6 cm in length and 5 mm in thickness. A cylindrical gel 6 mm in diameter and length was also prepared to measure the equilibrium swelling diameter of the gel.

Measurement of swelling properties of the gel

The equilibrium-swelling diameter was measured in water [12]. A gel of the length equal to the diameter 6 mm was placed in a rectangular cell, made of acrylic resin and filled with deionized water. The cell was immersed in a water bath at 10 °C. The swelling diameter was measured using a cathetometer after the gel swelled to equilibrium. The temperature of water bath was then increased to the desired temperature, and the equilibrium diameter of the gel was measured in the same way as above. The procedures were repeated up to 50 °C.

The internal structure of the gel was observed by scanning electron microscopy (SEM). The gel was allowed to shrink at a desired temperature, and was then lyophilized to prepare a sample for observation.

Dewatering of organic slurry with the gel

The water in which rice was washed was used as the organic slurry. The slurry, the waste from a rice-washing machine, was supplied by the Satake Corp. (Higashi-Hiroshima, Japan). The water content of the slurry was about 91 %. The slurry contained proteins, lipids, sugars, ash and dietary fibers. Before dewatering, the gel was allowed to shrink at 50 °C in water, and the excess surface water was removed by blotting with paper. The gel was then left undisturbed at room temperature (*ca.* 20 °C) for about one hour. A section of poly(vinyl chloride) pipe (3 cm in length, 52 mm inner diameter) was placed on the upper side of the gel to keep the slurry on the gel surface. The dewatering areas were 40.1 cm^2. A small amount of slurry was poured into the pipe and water was absorbed through the upper side of the gel. The dewatered cake was removed from the gel after a specified time and dried in an oven at 100 °C for a day. The water content of the dewatered cake was determined from the difference between the weight of the dewatered cake before and after drying.

Measurement of amount of water in the gel

Five pieces of the gels 30 mm in length, 30 mm in width and 5 mm thick were prepared. The surface of each gel was covered with a membrane filter 30 µm in thickness, with a 0.5 µm pore size to separate small particles from the slurry water for accurate estimation of the weight of water. Three g of slurry was dewatered for each gel for periods of 5, 10, 30, 60 and 120 min. After dewatering, samples were collected from different layers of the gel. The gel was cut into 5 mm squares, then sliced into four layers 1.2 mm in thickness to give samples as shown in Fig 1. Each sample was dried at 100 °C overnight. The amount of water in each sample was calculated using the following equation;

$$\alpha = (W_{\mathrm{gel}} - W_{\mathrm{dry\ gel}}) / W_{\mathrm{dry\ gel}} \text{ [g water/g dry gel]} \qquad (\mathbf{1})$$

where W_{gel} is the weight of the gel and $W_{\mathrm{dry\ gel}}$ is the dry weight of the gel.

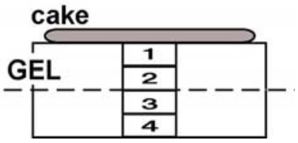


Figure 1. Position of layers of each sample.

Results and Discussion

Effect of crosslinker concentration on swelling and dewatering rate

The concentration of crosslinker has a significant effect on the degree of swelling of porous as well as non-porous gels. Figure 2 shows the effect of crosslinker concentration on the swelling diameter of porous gels in water. The gels were prepared using various concentrations of crosslinker. The swelling diameter increased with decreasing crosslinker concentration, suggesting that a gel with a low crosslinker concentration would absorb more water than a gel with a high crosslinker concentration. Thus, the water absorption capacity of the gel increased with decreasing crosslinker concentrations.

Figure 3 shows the effect of crosslinker concentration on dewatering rate of the slurry. The water content of the slurry on a gel prepared with the crosslinker concentration 60 mol·m^{-3} (G2) decreased faster than that of a gel with the crosslinker concentration 20 mol·m^{-3} (G1). We previously reported that the absorption rate increased with increasing concentration of crosslinker because a porous structure develops with increasing the concentration of crosslinker and the swelling rate of porous gel increases with the development of a porous structure [13]. However, the water content of the slurry on the gel prepared with a crosslinker concentration of 120 mol·m^{-3} (G3) decreased slower than that of gel G2.

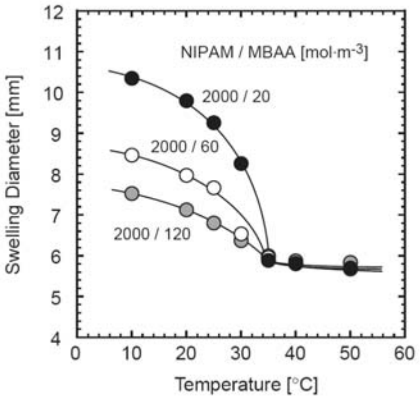


Figure 2. Effect of crosslinker concentration on swelling diameter.

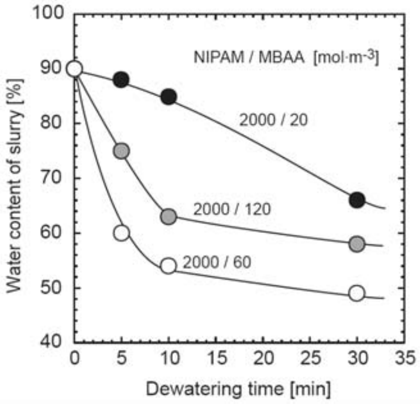
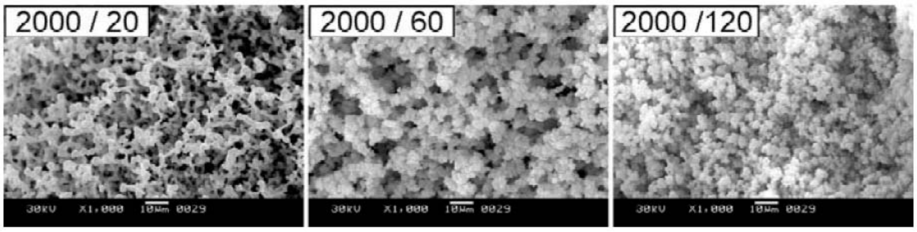


Figure 3. Effect crosslinker concentration on dewatering rate.

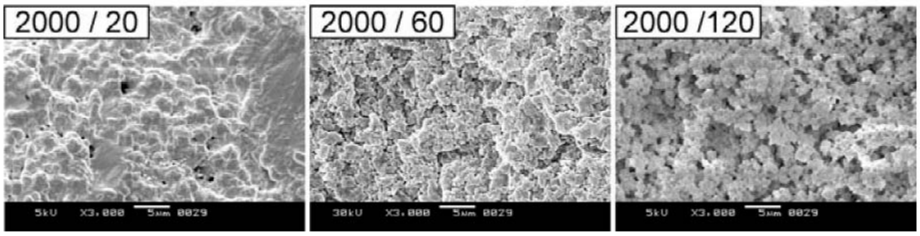
The internal structures of these gels were observed by SEM. Figure 4 shows SEM photographs of the porous structure of the gels that had been allowed to shrink at 50 °C. The results show that the number of the gel particles increased and that the pore size decreased with increasing crosslinker content.

Figure 5 shows SEM photographs of the gel just before the dewatering procedure. The gel particles absorbed water in the pores and, as a result, the pore size decreased because they had been cooled to room temperature. Most of the pores disappeared in gel G1. These observations suggest that the absorption rate of gel G1 decreased as the result of a decrease in the size of pore channel through which the water was transferred. On the other hand, gel G3 showed a lower water absorption rate in spite of its well-developed porous structure because the degree of swelling of gel particles decreased with increasing concentration of the crosslinker. As a result, the water-absorption rate of the gel decreased despite its porous structure. Consequently, an optimum crosslinker concentration exists in which the porous structure and the degree of swelling are both maintained for slurry dewatering by the porous thermosensitive gel.



(a) (b) (c)

Figure 4. SEM photographs of the porous structure of the gels prepared with different crosslinker concentrations: (a) G1: 20 mol·m^{-3}, (b) G2: 60 mol·m^{-3}, (c) G3: 120 mol·m^{-3}.



(a) (b) (c)

Figure 5. SEM photographs of the gel just before the dewatering procedure at 20°C: (a) G1: 20 mol·m^{-3}, (b) G2: 60 mol·m^{-3}, (c) G3: 120 mol·m^{-3}.

Effect of polymer concentration on swelling and dewatering rate

Porous gels with three different polymer concentrations were prepared to examine the effect of polymer concentration on absorption rate. The crosslinker-to-monomer ratio of molar concentrations in each gel was 0.03. Figure 6 shows the swelling diameters of the gels in water at various temperatures. The swelling diameters of these gels were almost equal at all temperatures examined. This suggests that the increase in monomer concentration resulted in an increase in the concentration of the polymer in the gel at the same temperature. The polymer concentration in the gel is determined by the volume fraction of the polymer in the gel, β. The ratio β was calculated from the equilibrium volume of the gel in water, V_{gel}, the density of water, ρ and the weight of the gel, W_{gel} as follows:

$$\beta = \{V_{gel} - (W_{gel} - W_{dry\ gel})\cdot\rho^{-1}\}\cdot V^{-1}_{gel} \qquad \mathbf{(2)}$$

where $W_{dry\ gel}$ is the weight of dry gel.

Table 2. Volume fraction of the polymer in the gel.

Monomer concentration [mol·m^{-3}]	2000	2250	2500
Volume fraction at 50 °C	0.245	0.281	0.303
Volume fraction at 20 °C	0.0924	0.107	0.115

Table 2 shows the volume fraction of polymer in the gel in water at 50 °C and 20 °C. This result shows that the polymer ratio increased with an increase in the monomer concentration. Figure 7 shows the effect of the polymer concentration on absorption rate. In the beginning, within 10 minutes, the water content of the slurry on the gel prepared with a low monomer concentration decreased more rapidly than that on a gel with a high monomer concentration. However, the latter water content decreased more rapidly than the former later on. The absorption rate increased with the development of a porous structure in the gel, as described above. The internal structures of these gels were observed by SEM.

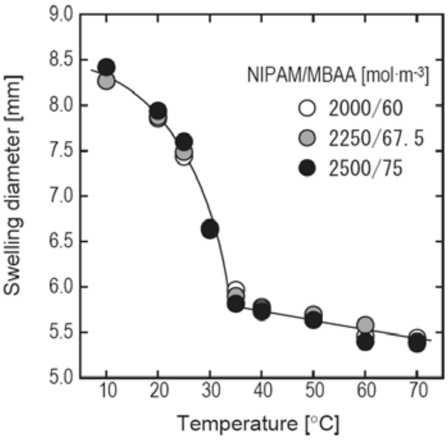


Figure 6. Swelling diameters of the gels at various temperatures.

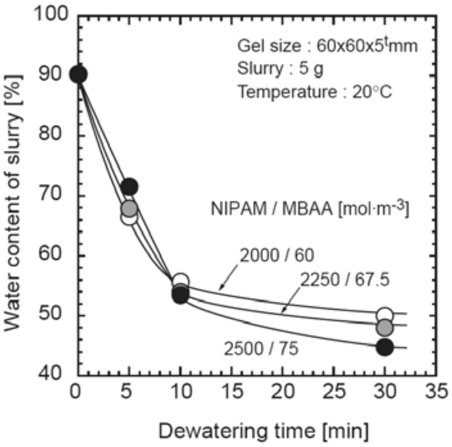


Figure 7. Effect of the concentration of polymer on the absorption rate.

Figure 8 shows SEM photographs of the porous structure of gels prepared with different monomer concentrations. The diameters of the gel particles and the pore size decreased with an increase in monomer concentration. Figure 9 shows SEM photographs of the gel that absorbed water at 20 °C. When the gel particles absorbed water, the pore size decreased. Most of the pores disappeared especially in the case of gel G6 at 20 °C. These observations suggest that the absorption rate decreased with increasing monomer concentration because the decrease in the pore size resulted from an increase in the volume fraction of the polymer as shown in Table 2. On the other hand, the water content decreased to the largest extent in the case of the slurry that was dewatered using gel G6. These results suggest that the absorption rate is influenced by the porous structure of the gel and that the amount of water absorbed by the gel is influenced by the polymer concentration of the gel.

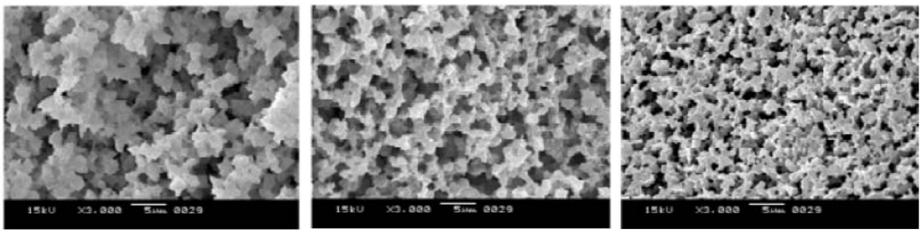

(a) (b) (c)

Figure 8. SEM photographs of the porous structure of gels prepared with different monomer concentrations: (a) G4: 2000 mol·m^{-3}, (b) G5: 2250 mol·m^{-3}, (c) G6: 2500 mol·m^{-3}.

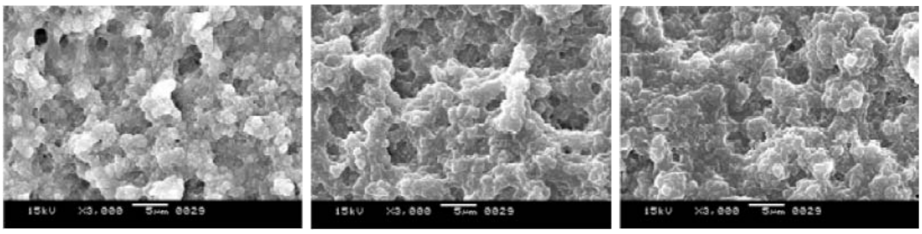
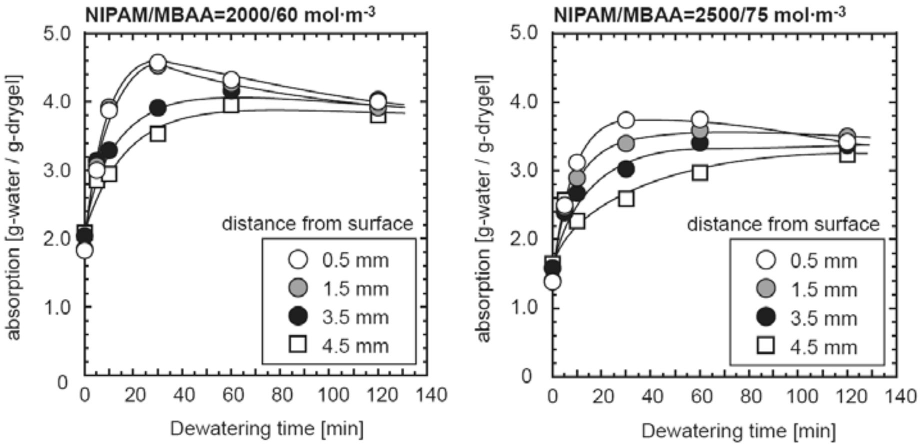

(a) (b) (c)

Figure 9. SEM photographs of the gel at 20°C: (a) G4: 2000 mol·m^{-3}, (b) G5: 2250 mol·m^{-3}, (c) G6: 2500 mol·m^{-3}.

Effect of polymer concentration on water absorption and transfer in the gel

From the results described above, the absorption of water by a porous gel consists of two steps, water transfer through the pore and penetration of water into the gel particle. The water absorption rate was measured to evaluate the effect of polymer concentration in the gel on water absorption. Smaller-size gels (3 cm x 3 cm) prepared with different monomer concentrations (2000 mol·m^{-3} (G4) and 2500 mol·m^{-3} (G6)) were used.

The amount of water in the gels at a certain distance from the dewatering surface was measured as a function of time. Figures 10a and 10b show the time course for the water content of the gels measured in different layers of each gel (a: G4, b: G6). The initial distances of each layer from the gel surface were 0.5 mm, 1.5 mm, 3.5 mm and 4.5 mm, as shown in Figure 1. There were no differences between the initial water contents in any of these layers for each gel. The initial water content of gel G4 was higher than that of gel G6 because of its lower polymer concentration, as shown in Table 2. The water content of the top layer of gel G4 increased faster than that of gel G6, indicating that the water-absorption rate of the gel from the slurry decreased with increasing polymer concentration in the gel. The increase in polymer concentration reduced the rate of penetration of water into the gel particles although the gel had developed a porous structure. On the other hand, the amount of water absorbed by each gel was 2.125 g (G4) and 2.292 g (G6). The average water content of the gel was 79.7 % (G4) and 77.2 % (G6), while the average water content of the dewatered slurry was 60.8 % (G4) and 59.8 % (G6). Both were lower than the water contents of the gels. This shows that the NIPAM polymer has a stronger affinity to water than the solid components in the slurry, suggesting that an increase in the volume fraction of the polymer in the gel provides higher absorption of water for the gel. As a result, the uptake of water by the gel from the slurry increased with increasing in the polymer concentration in the gel.



(a) (b)

Figure 10. Time course of the water content in the gels measured in different layers (a) 2000 mol·m^{-3} (G4), (b) 2500 mol·m^{-3} (G6).

The water content of the upper two layers adjacent to the slurry initially increased and then gradually decreased, while those of the bottom ones increased gradually. This indicates that the amount of water absorbed by the gel from the slurry decreased with time, while the absorbed water moved to the bottom layers. The differences in water contents between those layers decreased to a minimum again, suggesting that the water transfer between the layers stopped.

Figure 11 shows the effect of polymer concentration on the average water transfer rate between those layers. The rates were calculated from the amount of water absorbed by each layer of the gels in a defined period, 10 min, 20 min, 30 min and 60 min of dewatering. The time in the middle of each period represented each period. All the water transfer rates decreased with time. When the slurry was dewatered with the gel G4, the absorption rates of the upper two layers were higher than those for the bottom layers; then they decreased and became smaller than those of bottom layers in the course of the dewatering. The rate of water transfer from the slurry to the top layer and from the top layer to a second layer decreased faster than those between the bottom layers because of the decrease in the pore size due to swelling of the gel. The water transfer between bottom layers slowly decreased because the bottom layers of the gel did not swell sufficiently to prevent water from being transferred.

When the slurry was dewatered with gel G6, the rates of absorption of the upper two layers were higher than those for the bottom layers throughout the dewatering process. This suggests that the water transfer from the slurry to the top layer and between the layers gradually decreased because gel G6 swelled more slowly than gel G4 and the pores of gel G6 remained, permitting the transfer of water through them. The polymer concentration of gel G6 was higher than that of gel G4 and the high polymer

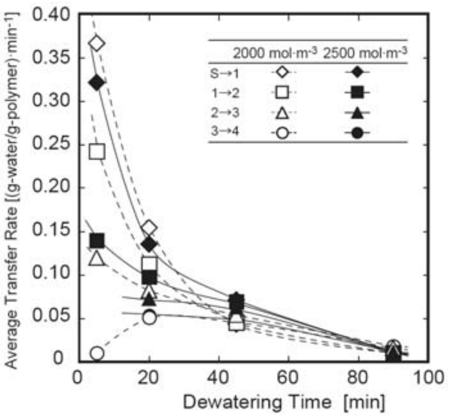


Figure 11. Average water absorption rates between layers: S-1: from slurry to layer 1, 1-2: from layer 1 to layer 2, 2-3: from layer 2 to layer 3, 3-4: from layer 3 to layer 4, open keys: 2000 mol·m^{-3} (G4), closed keys: 2500 mol·m^{-3} (G6).

concentration reduced the rate of penetration of water into the gel. Therefore, the water absorption rate of gel G6 was smaller than that of gel G4.

Consequently, a high polymer concentration with an adequate crosslinker concentration of gel is needed for dewatering the slurry because an increase in polymer concentration provides the gel with a high osmotic pressure of water. The water absorption rate decreased slightly because of the decrease in pore diameters resulting from the increase in the volume fraction of the polymer in the gel.

Conclusions

A reinforced thermosensitive porous gel was prepared for dewatering organic slurries and the effects of preparation conditions, such as the concentration of crosslinker and polymer in the gel on absorption rate were examined. The findings showed that the water absorption rate was influenced by the porous structure and the polymer concentration in the gel. The absorption of water by the porous gel consists of two steps, transfer of water through the pore and penetration of water into the gel. Water transfer was improved by the development of channels of connected pores in the gel, i.e. a porous structure, which could be developed by increasing the crosslinker concentration. The increased crosslinker concentration prevents the gel from swelling, and maintains the structure of the channel, which enables water to transfer. However, an increase in crosslinker concentration decreases the water absorption rate of the gel because the increased crosslinker concentration restricts the degree of swelling of the gel. The decrease in crosslinker concentration, on the contrary, increases the water absorbing capacity, but the porous structure of the gel is likely to diminish by swelling and it decreases the transfer of water through pore channels. Therefore, there is an optimum crosslinker concentration for maintaining both the porous structure and a sufficient degree of swelling for dewatering by the porous gel.

When a porous gel was prepared with an optimal crosslinker-monomer ratio, the equilibrium swelling degrees of the gels in water at a certain temperature were the same among gels of different polymer concentrations. Therefore, the volume water absorbing capacity increased with increasing polymer concentration of the gel because of an increase in the osmotic pressure of water. The water absorption rate decreased slightly with increasing polymer concentration of the gel because the increase in volume fraction of the polymer decreased the pore size of the gel. Consequently, the water absorption rate is determined by the porous structure and water absorption capacity is determined by the volume fraction of the polymer in the gel. A high polymer concentration with the optimal crosslinker-polymer ratio is preferable in preparing porous thermosensitive gels for use in the slurry dewatering.

Acknowledgements. The authors thank the Kohjin Co., Ltd. (Tokyo) for the supply of NIPAM monomer. We also thank the Shokkyo Co., Ltd. (Hiroshima) and the Satake Co., Ltd for the supply and analysis of the organic slurry. This research contains a part of the results of the Regional Research & Development Consortium Project supported by the Chugoku Bureau of Economy, Trade and Industry.

References

1. Freitas RFS, Cussler EL (1987) Sep Sci Technol 22:911
2. Trank SJ, Johnson DW, Cussler EL (1989) Food Technol 6:78
3. Sassi AP, Shaw AJ, Han, SM, Blanch HW, Prausnitz JM (1996) Polymer 37:2151
4. Hirasa O (1986) Kobunshi 35:1100
5. Kishi R, Hirasa O, Ichijo H (1997) Polym Gels Networks 5:145
6. Huang X, Akehata T, Unno H, Hirasa O (1988) J Chem Eng Jpn 21:10
7. Huang X, Akehata T, Unno H, Hirasa O (1988) J Chem Eng Jpn 21:651
8. Huang X, Akehata T, Unno H, Hirasa O (1989) Biotechnol Bioeng 34:102
9. Akehata T, Mochizuki M, Kawakami T, Hayashi A (1996) Preprints of the 29th Autumn Meetings of the Society of Chemical Engineers, Japan 2:164 (in Japanese)
10. Kabra BG, Gehrike SH (1991) Polym Commun 32:322
11. Wu XS, Hoffman AS, Yager P (1992) Polym Sci A 30:2121
12. Gotoh T, Nakatani Y, Sakohara S (1998) J Appl Polym Sci 69:895
13. Gotoh T, Okamoto H, Sakohara S (2004) J Chem Eng Jpn 37:597
14. Tanaka T (1981) Sci Am 1:124
15. Flory PJ (1953) Principles of Polymer Chemistry Cornell Univ Press, New York