UV-irradiation Effects on the Properties of *poly*-Acrylamide/Sodium Acrylate Gel

Kazuhiro Hara, Yoshio Uemoto, Naohiro Ueno,
Koutaro Terayama and Satoru Yoshioka

¹Research Institute of Environment for Sustainability,
Faculty of Engineering, Kyushu University,
744 Motoooka, Fukuoka 819-0395 Japan

Fax: 81-92-802-3485, e-mail: khara@nucl.kyushu-u.ac.jp

In the present study, the authors have investigated how the UV-ray irradiation affects the surface condition of wet and dehydrated poly(acrylamide/sodium acrylate) (PAAm/SA) gels. With large amounts of the UV-ray dosage, the wet PAAm/SA gel readily disintegrates to wreak the surface erosion while the dehydrated gel exhibits considerable turbidness in spite of no remarkable change in outline. Besides, even with the smaller dosage spawning no appreciable change only by the UV-ray irradiation, some of the wet PAAm/SA gels turn significantly opaque by putting an aqueous CuCl_2 solution on the surface, which indicates the breakup of the surface layer of the wet PAAm/SA gel.

Key words: hydrogel, heavy metal, UV, turbid

1. INTRODUCTION

Some hydrogels show very interesting and useful properties through the interaction between intimately-intertwined ingredients, a 3-dimensional network and solvent [1]. One of the well-known phenomena is the volume phase transition, a drastic and large volume change with the slight shift of environmental conditions such as pH, hydrophobicity of the solvent, temperature, electric field and so on. In the process, the ionizing groups in the side-chains dangled from the gel network affect so much the transition features such as significant amplification of the volume change degree [1-5]. In addition to the influence on the volume phase transition, another useful functionality is developed by introducing the ionizing group in the network, to which the authors have been paying attention, the multivalent-ion capturing functionality. Before the authors' studies, developed was a heavy-metal ion detector utilizing an interpenetrating-network hydrogel made of poly(vinyl alcohol) and *N*-isopropylacrylamide/acrylic acid, which detects a heavy metal ion via the shift of the volume-phase-transition temperature [6]. However, the detector was not able to show how much the heavy-metal amount the gel can adsorb. In these circumstances, the authors have been focusing attention on the adsorbable quantity of the heavy-metal-capturing gels aiming at the realization of the high-efficient heavy-metal recovery gels [7-18].

First, the authors started the investigations of heavy-metal-cation capturing properties of some ionized hydrogels such as sodium acrylate/acrylamide (SA/AAm) and sodium carboxymethylcellulose (CMC-Na) gels; and they found that the ionized gels can capture cupric ion to the extent of ~20wt% of their network, which is considerably large compared with other adsorbents such as zeolites and ion-exchange resins (Fig.1) [7,8]. In addition

to the heavy-metal-cation capturing hydrogels, the authors have been also investigating heavy-metalanion capturing hydrogels because there are many harmful heavy-metal anions in the environment such as $\text{Cr}_2\text{O}_7^{2-}$; and they found that some heavy-metal-anion adsorbing hydrogels show larger heavy-metal capturing efficiencies than SA/AAm and CMC-Na gels [9-14]. Moreover, recently, the authors demonstrated the possibility of the high-efficient heavy-metal-recycle process utilizing these hydrogels [15-18].

Though some hydrogels show the high heavy-metal capturing efficiencies and are expected to be utilized for the heavy-metal recycle as mentioned above, the small

Fig. 1

The CuCl_2 concentration dependence of the Cu(II) weight adsorbed by the several SA/AAm gels per 10 g of the respective pre-gel solutions [7,8]. The symbols, ●, □ and * denote the data of the SA/AAm gels with molar ratios SA:AAm=1:6, 2:5, 3:4, respectively.

solvent-diffusion rate constitutes barriers to such a utilization. Therefore, the authors have been also investigating the methods which remedy these situations. In the previous studies, the authors made attempts to enlarge the solvent-diffusion rate by forming porous structures by adding excessive amounts of cross-linker [19] or by preparing them above room temperature after adding excess amounts of polymerization accelerator [20]; however the inhomogeneous gels made by these methods are too hard to be utilized for the present purpose. The authors' third method for introducing the inhomogeneity into the hydrogels is conducting a solvent substitution treatment as a post-gelation process, which enables marked acceleration to the swelling process [21].

In the present study, as the forth method, the authors utilized the photolysis of an ultraviolet (UV) light for creating the higher performance gel. By the present method, a crosslink concentration gradient, so as to be low near the surface and also to be high its inside, was supposed to be easily introduced because the UV-ray can effectively cut the polymer chain with an appropriate dosage; and, at the same time, the UV-ray intensity decreases with penetrating depth.

2. EXPERIMENTALS AND RESULTS

Sample Preparation and UV-irradiation equipment

The aqueous solution of 200 mM of SA, 500 mM of AAm and 12.3 mM of *N,N'*-methylenebisacrylamide (BIS, cross linker) was prepared as the pregel solution, which was left intact for 24 hrs at 60 °C after adding 2.54 mM of ammonium persulfate (polymerization initiator). After the period, several tiled portions with a dimension of $\sim 15 \times 15 \times 4$ mm³ were cut out from the lump of the PAAm/SA gel. Then the small gel pieces were put in pure water in order to wash out unreacted ingredients; in the process, the volume of the gel slips increased ~ 40 times to the extent of $\sim 50 \times 50 \times 15$ mm³ in dimension. After the rinsing process, some of them were used as wet specimens without further treatments; and the others had been dehydrated at 5 °C for 2 weeks in a refrigerator, by which the gels shrank to $\sim 1/9$ ($\sim 7 \times 7 \times 2$ mm³ in dimension).

In the present study, a high pressure mercury lamp with output of 100 W (HANDY CURERUB Handy 100, SEN LIGHTS Co.,Ltd.) was utilized as a UV light source of which the intensity is 170 mW/cm² and the effective UV wave-lengths are 318 and 365 nm.

Occurrence of White Turbidity

in Dehydrated PAAm/SA Gel caused by UV-ray

The half of a dehydrated PAAm/SA gel specimen ($\sim 7 \times 7 \times 2$ mm³ in dimension) was covered with an aluminum foil; and UV-light had been irradiated to the specimen for 10 hrs. After the period, the aluminum foil was removed and the difference between the masked and unmasked areas was examined in order to investigate the UV-ray-irradiation effect.

Figure 2 shows the experimental features of a dehydrated PAAm/SA gel during the UV-ray-irradiation. As can be easily seen from the figure, the unmasked region of the dehydrated PAAm/SA gel turned opaque while the other masked area showed no remarkable change in comparison with the dehydrated gel before the UV-ray irradiation.

Fig. 2

UV-ray irradiation Effect on a dehydrated PAAm/SA gel. The half of the dehydrated gel specimen was covered with an aluminum foil and UV-light had been irradiated to the specimen for 10 hrs. The UV-ray irradiated side becomes opaque. See also text.

Fig. 3

A groove formation on a wet PAAm/SA gel surface by UV-ray irradiation in the shape of the aperture in a covering aluminum foil. The depth of the groove increased with the exposure period as shown in Fig. 4. See also text.

Fig. 4

The UV-ray-exposure period dependence of the digging depth on the surface of a PAAm/SA gel. The digging rate is accelerated with increasing UV-ray irradiation period. See also text.

Degradation of Wet PAAm/SA Gel by UV-ray

The UV-ray irradiation to the wet PAAm/SA gels for several periods, 20, 40 and 60 min, had been performed after covering their surface ($\sim 50 \times 50 \times 15$ mm³ in dimension) with aluminum foils with a slit of 5 mm in the center.

By the UV-ray irradiation, a groove in the shape of the slit in the aluminum foil was etched on its surface by the photodegradation of the wet PAAm/SA gel as shown in Fig. 3. With increasing the UV-ray irradiation period, the depth of the groove became larger. Figure 4 describes the UV-ray-irradiation-period dependence of the digging depth on the surface of the hydrogel. As can be easily seen from the figure, the digging rate of the groove is accelerated with increasing UV-ray irradiation period.

Property Changes of UV-irradiated Wet PAAm/SA Gel Caused by Heavy-Metal Capturing

The surface of the wet PAAm/SA gel was covered with an aluminum foil with a rectangular window of 8 mm in width in its midst (Fig. 5(a)). Then the UV-ray irradiation to the masked specimen had been performed for 15 min being shorter than that with which the groove in the wet gel appeared in the previous experiment. After the UV-ray irradiation, the aluminum foil was removed and a small amount of aqueous CuCl_2 solution (100 mM, 5 mL) was poured on the specimen surface. Immediately after pouring the aqueous CuCl_2 solution, the UV-irradiated surface area turned opaque as shown in Fig. 5(b). After the procedure, in a short while, the specimen was put into a beaker filled with aqueous CuCl_2 solution (100 mM, 50 mL) and had been left intact for 24 hrs. After then, the almost whole parts of the specimen shrank so much being the opaqueness of the turbid region unchanged (Fig. 5(c)).

Phase Contrast Microscope Observation of the Heavy-Metal Adsorbed PAAm/SA Gel across the Regions having been UV-irradiated and without UV-irradiation

Successively, the phase contrast microscope observation was carried out in order to examine more clearly the difference between the UV-ray irradiated and unirradiated regions observed in the previous section. With covering the half of the wet PAAm/SA gel specimen by the aluminum foil, the UV-irradiation was performed for 15 min. Then, after removing the aluminum foil, the gel specimen was immersed in the aqueous sodium chloride solution (100 mM, 5 mL) for 24 hrs. After the period, the gel specimen was observed with a phase contrast microscope.

Figure 6 shows the phase contrast microscope image across the boundary of the UV-ray irradiated and unirradiated area. As can be easily seen from the figure, there are characteristic corrugated patterns in the unirradiated region while no noticeable structures are observed in the UV-ray irradiated area.

Turbidimetric Measurements of Heavy-Metal Capturing Wet PAAm/SA Gel after UV-irradiation

For more quantitative investigation on the above-mentioned clouding properties, measured were the transmitted light spectra through the several wet PAAm/SA gels with different UV-ray irradiation periods. Each the fully swollen gel specimen was exposed to UV-light for a period in a range 0–15 min. Then, the specimens were washed in pure water for 24 hrs. After washing, each the UV-ray irradiated specimens was put in a beaker filled with 50 mL of 100 mM CuCl_2 aqueous solution. After left intact for 24 hrs, the gels were taken out from the

Fig. 5

The effect of UV-ray irradiation on the Cu adsorbing feature of PAAm/SA gel. (a) An Al foil with an apertured was put on the gel before UV-ray irradiation. (b) The area UV-ray-irradiated for 15 min became turbid by dropping a small amount of aqueous CuCl_2 solution. (c) The parts other than the UV-ray irradiated area shrank by dipping in aqueous CuCl_2 solution. See also text.

Fig. 6

The phase contrast microscope images across the boundary of UV-ray irradiated and unirradiated areas observed after immersed in CuCl_2 aqueous solution for 24 hrs. The unirradiated area shows corrugated patterns. See also text.

beaker and their thicknesses were measured.

Then both of the specimen and the surrounding aqueous CuCl_2 solution were put into a spectrophotometer cell. With arranging each the specimen perpendicular to an incident light beam, the transmitted light spectrum through the gel specimen in the aqueous CuCl_2 solution was measured by a spectrophotometer

(PD303, APOL Co., Ltd.) in a wavelength range from 340 to 1010 nm with a resolution of 10 nm. Then, the transmitted-light spectrum of the aqueous CuCl_2 solution was also measured after removing the gel specimen from the spectrophotometer cell. With these spectrum data, calculated were the wavelength dependence of the light transmissivity of the gel specimens.

Fig. 7

The light-transmissivity spectra at 1 mm of the PAAm/SA gels having been immersed in aqueous CuCl_2 solution for 24 hrs after the UV-ray irradiation for different periods from 0 to 15 min. See also text.

Figure 7 shows the light-transmissivity spectra of the PAAm/SA gels having been immersed in aqueous CuCl_2 solution for 24 hrs after the UV-ray irradiation for different periods from 0 to 15 min. As can be easily seen, each the light-transmissivity spectrum has a broad mound-like structure with a summit around 500 nm. The shapes of the light-transmissivity spectra are not affected so much by the UV-irradiation periods; on the other hand, the spectrum intensities increase considerably with the UV-ray exposure periods.

3. DISCUSSIONS

In the present study, the potent influences of the UV-light on the surface properties have been revealed. The emergence of the opaqueness in the dehydrated PAAm/SA gel and the erosion of the wet gel shown in Figs. 2 and 3 demonstrate clearly the sharp breaking of the network structure in the gel. The acceleration of the digging rate shown in Fig. 4 can be simply explained by the elevation of the inner-part UV-light intensity caused by the collapsing and sinking specimen-surface during the UV-light exposure period if the penetration depth of the UV-light exceeds the thickness of the gel specimen.

The surface property modifications caused by the relatively smaller UV-ray dosage shown in Figs. 5 and 7 are interesting from a viewpoint of the utilization of the surface functionality. Only by the small-dosage UV-ray irradiation, there is no noticeable appearance change; however, then, by applying aqueous CuCl_2 solution on the UV-ray irradiated surface, there occurs a significant turbidity. This result indicates that the UV-ray irradiated gel undergoes a very minute structural destruction on the surface, and then by applying Cu^{2+} , the coagulation of the hanging fractions on the gel surface occurs by the

linkage formation mediated by Cu^{2+} , namely with the chelation formation via Cu^{2+} .

During the process of the volume phase transition, it is well-known that some ionized gels exhibit wrinkled surface patterns like those shown in the lower part of Fig. 6 caused by the counteraction between elasticity and the force which causes nonmarginal volume change [1]. The disappearance of the corrugated pattern in the UV-ray irradiated area in upper left part of Fig. 6 indicates that the surface structure which generates the elasticity can be decoupled by the UV-ray there. Such an estimation coincides with that suggested by the opaqueness occurrence (shown in Fig. 5) in the UV-ray irradiated area by applying Cu^{2+} mentioned in the previous paragraph. The detail investigations are in progress.

REFERENCES

- [1] T. Tanaka, *Sci. Am.* 244, 124 (1981).
- [2] T. Tanaka, *Phys. Rev. Lett.*, 45, 1636 (1980).
- [3] T. Tanaka, *Phys. Rev. Lett.*, 40, 820 (1978).
- [4] S. Hirotsu, Y. Hirokawa, and T. Tanaka, *J. Chem. Phys.*, 87, 1392 (1987).
- [5] S. Hirotsu, *Phase Transitions*, 47, 183 (1994).
- [6] D.K. Jackson, S.B. Leeb, A. Mitwalli, D. Fusco, C. Wang, and T. Tanaka, *J. Intell. Mater. Syst. Struct.*, 8, 184 (1997).
- [7] K. Hara, M. Iida, K. Yano and T. Nishida, *Colloids and Surfaces B*, 38, 227 (2004).
- [8] K. Hara, M. Yoshigai and T. Nishida, *Trans. Mat. Res. Soc. Jpn.*, 30, 823 (2005).
- [9] K. Hara, M. Yoshigai and T. Nishida, *Trans. Mat. Res. Soc. Jpn.*, 31, 815 (2006).
- [10] K. Hara, M. Yoshigai and T. Nishida, *Trans. Mat. Res. Soc. Jpn.*, 32, 819 (2007).
- [11] K. Hara, S. Yoshioka, A. Nishida, M. Yoshigai and T. Nishida, *Trans. Mat. Res. Soc. Jpn.*, 33, 369 (2008).
- [12] K. Hara, S. Yoshioka, A. Nishida, M. Yoshigai and T. Nishida, *Trans. Mat. Res. Soc. Jpn.*, 33, 455 (2008).
- [13] K. Hara, S. Yoshioka, A. Nishida, M. Yoshigai and T. Nishida, *Trans. Mat. Res. Soc. Jpn.*, 33, 463 (2008).
- [14] A. Nishida, N. Kawamura, T. Nishida, S. Yoshioka and K. Hara, *Trans. Mat. Res. Soc. Jpn.*, 33, 459 (2008).
- [15] K. Hara, N. Kawamura, D. Yamada, S. Yoshioka, T. Nishida, *Trans. Mat. Res. Soc. Jpn.*, 34, 489 (2009).
- [16] N. Kawamura, D. Yamada, T. Nishida, S. Yoshioka, K. Hara, *Trans. Mat. Res. Soc. Jpn.*, 34, 493 (2009).
- [17] K. Hara, N. Kawamura, K. Nagamatsu, D. Hisajima, M. Yoshigai, S. Yoshioka and T. Nishida, *Trans. Mat. Res. Soc. Jpn.*, 34, 497 (2009).
- [18] K. Hara, N. Kawamura, K. Nagamatsu, D. Hisajima, M. Yoshigai, S. Yoshioka and T. Nishida, *Trans. Mat. Res. Soc. Jpn.*, 34, 501 (2009).
- [19] K. Hara, Y. Sueyoshi, M. Sugiyama and T. Tanigawa, *Trans. Mat. Res. Soc. Jpn.*, 31, 89 (2006).
- [20] K. Hara, K. Yanagihara, T. Tanigawa, A. Nishida and S. Yoshioka, *Trans. Mat. Res. Soc. Jpn.*, 32, 831 (2007).
- [21] K. Hara, T. Tanigawa, K. Yanagihara, A. Nishida and S. Yoshioka, *Trans. Mat. Res. Soc. Jpn.*, 32, 795 (2007).

(Received June 28, 2010; Accepted August 2, 2010)