

Photoinduced Surface Crosslinking of Superabsorbent Polymer Particles

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ABSTRACT: Superabsorbent polymer particles, consisting of partly neutralized, slightly crosslinked poly(acrylic acid), have been surface-crosslinked photochemically. Surface crosslinking is required for many applications of superabsorbent polymers, such as disposable diapers, to control the flow and absorption of liquids in the gel bed. Photoinduced surface crosslinking has been achieved under UV irradiation (200–300 nm) with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as a photoactivated crosslinking agent. In comparison with the currently used thermal ester bridging method for surface

crosslinking, the new photochemical method generates superabsorbent particles with superior properties, such as an improved flow of liquid through the gel bed, which utilizes the entire gel bed. These improved properties have been shown by water absorption capacity studies, fluid flow dynamics, environmental scanning electron microscopy, and low-energy ion-scattering studies. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2163–2170, 2009

Key words: crosslinking; hydrophilic polymers; swelling

INTRODUCTION

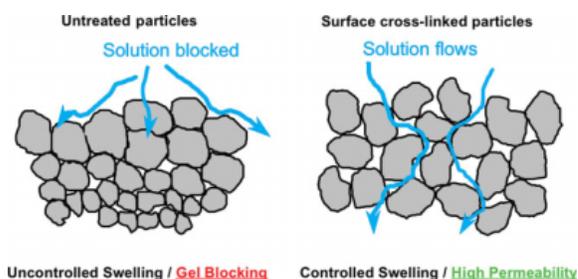
Superabsorbent polymers are lightly crosslinked networks of hydrophilic polymers that absorb up to 1000 g of water per gram of polymer and up to about 100 g of dilute salt solutions per gram of polymer.^{1–3} Since their introduction more than 30 years ago,⁴ superabsorbent polymers have been used in various products, such as water-absorbing materials in disposable diapers, water-swelling rubbers, water-blocking tapes, drug-delivery systems,⁵ soil additives for agriculture,³ cement,⁶ and sensors.⁷ The majority of superabsorbent polymers produced by industry are used in disposable baby diapers, with an annual production of about 1.3 million metric tons per year in global industry in 2005.⁸ As a superabsorbent material, partly neutralized, lightly crosslinked poly(acrylic acid) particles are used for diaper materials (gel bed). These particles are embedded into the gel bed and can absorb and hold about 20–40 mL of urine per gram of polymer.¹ A major challenge in the optimization of fluid collection is controlling the fluid flow in the gel bed. Untreated

particles tend to swell rapidly on the top layer of the gel bed and form an insulating (gel-blocking) layer, which inhibits the flow and absorption of fluid in the lower parts of the gel bed (Scheme 1, left). This gel blocking can cause the diaper to leak and lead to underuse of the absorption capacity of the gel bed.^{2,9} Surface crosslinking of the superabsorbent particles improves the flow significantly. The surface-crosslinked particles maintain their shape during the swelling process, which generates a less densely packed gel bed with air pockets, so the fluid can flow in a less restricted fashion (Scheme 1, right). This higher permeability allows for a more efficient use of the gel bed.

Currently, surface crosslinking of the superabsorbent particles [partially neutralized, lightly crosslinked poly(acrylic acid)] is achieved by the creation of ester or amide linkages between poly(acrylic acid) chains with polyols, alkylene carbonates, or oxazolidinone compounds (Scheme 2).^{10,11} However, relatively high temperatures (150–200°C) and long reaction times (30–60 min) are required for these reactions. These are conditions that are energy-consuming and not attractive for large-scale industrial production of superabsorbent materials. Therefore, an important challenge is to design more energy-efficient and faster crosslinking reactions. In this article, we report a photochemical surface crosslinking method that operates at room temperature, requires

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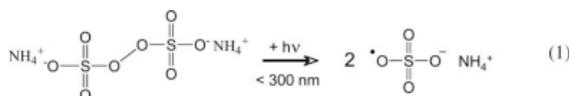


Scheme 1 Schematic representation of the swelling and flow of aqueous solutions through the (left) uncrosslinked and (right) surface-crosslinked superabsorbent polymer particles in the gel bed.

shorter reaction times, and generates superior superabsorbent particles; these are all attractive features for large-scale economic production.

RESULTS AND DISCUSSION

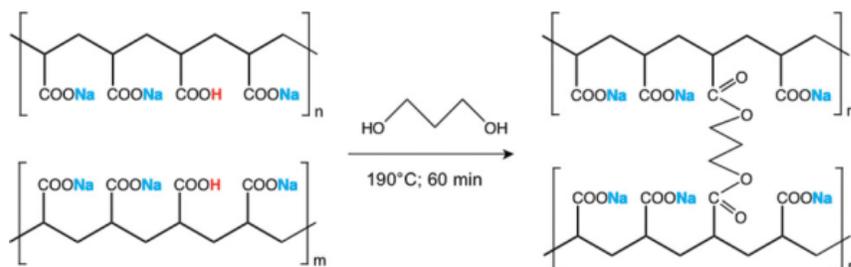
Ammonium peroxydisulfate [(NH₄)₂S₂O₈] was selected as a photoactivated crosslinking agent for the crosslinking of partially neutralized poly(acrylic acid).^{12–14} Upon irradiation (hν) at a wavelength shorter than 300 nm, (NH₄)₂S₂O₈ cleaves to yield two SO₄^{•−} radical anions [eq. (1)].^{15,16} The radical anions abstract hydrogen from organic molecules to generate very reactive carbon-centered radicals [R[•]; eq. (2)].¹⁶ In the absence of radical scavengers, the carbon-centered radicals combine to form nonradical products [eq. (3)]:



We used the reaction sequence of eqs. (1)–(3) to crosslink the superabsorbent polymer particle surfaces. In a typical experiment, the dry polymer particles were placed in a quartz flask and stirred thoroughly, and a small amount of an aqueous solution of (NH₄)₂S₂O₈ was added slowly. The amount of the added solution just wetted the surface of the particles but did not cause significant swelling of the particles. The particles were continuously stirred for 15 min to ensure a homogeneous coating of the particle surfaces with the (NH₄)₂S₂O₈ solution, and then the stirred particles were irradiated for 10 min with UV light.

The properties of the photochemically surface-crosslinked, thermally surface-crosslinked, and uncrosslinked particles are compared on the basis of their absorbance capacity for a salt solution (0.9% w/w NaCl in H₂O, a model system for urine) and saline permeability in Table I. A parameter that expresses the total amount of an aqueous salt solution that the particles can absorb is the centrifuge retention capacity (CRC). The untreated particles (sample 1) showed the highest CRC (CRC = 31). Surface crosslinking (thermal or photochemical: samples 4 and 2, respectively) reduced the total salt solution absorbency slightly (CRC = 27). However, in practical applications such as diapers, the gel bed is exposed to pressure due to the body weight of the baby. A parameter that takes this pressure into account is the absorbency under load (AUL): the absorbency is measured under a pressure of 0.7 psi. Under pressure, the untreated particles showed only a low capacity (AUL = 8). However, the thermally and photochemically crosslinked particles possessed a significantly higher capacity under pressure (AUL = 25 and 20, respectively).

Another parameter that is important for a high-performance superabsorbent polymer particle is the saline flow conductivity (SFC). As illustrated in Scheme 1, particles that maintain their shape during the swelling process are expected to show higher



Scheme 2 Example of the thermal surface crosslinking of the poly(acrylic acid) particles.

TABLE I
Properties of the Superabsorbent Poly(acrylic acid) Particles (70 mol % Neutralized)

Sample	Surface crosslinking	Acid	CRC (g/g) ^a	AUL (g/g) ^b	SFC (10 ⁻⁷ cm ³ s/g) ^c
1	None	—	31	8	0
2	UV ^d	—	27	20	26
3	UV ^d	HCl ^e	25	21	73
4	Thermal ^f	—	27	25	51

^a CRC of a 0.9% NaCl solution (error limit ± 0.5).

^b Error limit ± 0.5 .

^c Error limit ± 10 .

^d Peroxodisulfate solution: 2.5% (NH₄)₂S₂O₈, 8% H₂O [w/w based on the total weight of the poly(acrylic acid) particles]. UV irradiation time = 10 min.

^e Concentrated HCl solution [6% w/w based on the total weight of the poly(acrylic acid) particles] was added to the initiator solution that was used to coat the particles before irradiation.

^f Particles thermally surface crosslinked with aliphatic diols.

flow conductivity due to a looser packing of the swollen particles. Experimentally, the uncrosslinked particles showed essentially no flow conductivity (SFC = 0; Table I, sample 1), and this was caused by gel blocking (Scheme 1, left). Surface crosslinking (thermal or photochemical: samples 4 and 2, respectively) improved the flow conductivity significantly (SFC = 51 and 26, respectively). However, a higher flow conductivity was observed for the thermally crosslinked particles (SFC = 51) versus the photochemically crosslinked particles (SFC = 26), and this was probably caused by different types of crosslinks and by different degrees of surface crosslinking.

To achieve a higher degree of photoinduced surface crosslinking, which was expected to improve the flow conductivity (SFC), several parameters were varied, such as the addition of acids, the irradiation time, the addition of different peroxodisulfate counter ions (Na⁺ and NH₄⁺), and the addition of a dispersion agent such as poly(ethylene glycol) or poly(ethylene glycol) methyl ether (PEG-OMe). In one experiment, a small amount of acid (HCl) was added to the peroxodisulfate solution before the

solution was dispersed onto the particles before irradiation (Table I, sample 3). Although there was almost no change in the total water absorbency (CRC) and the capacity under pressure (AUL), the flow conductivity (SFC) improved significantly in comparison with the photochemically crosslinked particles without an acid (sample 2). The photochemically surface-crosslinked particles with an acid (sample 3) also outperformed the thermally surface-crosslinked particles (sample 2) with respect to the flow conductivity (Table I).

Table II shows the values of CRC, AUL, and SFC for superabsorbent particles, which were photochemically crosslinked with a different batch of superabsorbent particles with a higher degree of neutralization (75 mol %) of the carboxylic acid groups by NaOH. Therefore, a direct comparison of the data in Table I with Table II must be made, taking this factor into account. From the data in Table II (samples 2–4), it can be concluded that a decrease in the irradiation time by one-half or a decrease in the peroxodisulfate concentration by one-half had only negligible effects on the salt solution

TABLE II
Properties of the Superabsorbent Poly(acrylic acid) Particles (75 mol % Neutralized)

Sample	Composition of peroxodisulfate solution ^a	Irradiation time	Water content (%)	CRC (g/g) ^b	AUL (g/g) ^c	SFC (10 ⁻⁷ cm ³ s/g) ^d
1	—	—	8	35	8	0
2	2.5% (NH ₄) ₂ S ₂ O ₈ , 8% H ₂ O	10 min	14	26	19	28
3	5% (NH ₄) ₂ S ₂ O ₈ , 8% H ₂ O	10 min	14	24	20	48
4	5% (NH ₄) ₂ S ₂ O ₈ , 8% H ₂ O	5 min	14	25	19	21
5	5% Na ₂ S ₂ O ₈ , 8% H ₂ O	10 min	14	25	19	47
6	5% (NH ₄) ₂ S ₂ O ₈ , 8% H ₂ O	— ^e	13	31	8	0
7	5% (NH ₄) ₂ S ₂ O ₈ , 8% H ₂ O, 0.5% PEG-OMe	10 min	14	24	20	85

^a Weight/weight percentage based on the total weight of the poly(acrylic acid) particles.

^b CRC of a 0.9% NaCl solution (error limit ± 0.5).

^c Error limit ± 0.5 .

^d Error limit ± 10 .

^e The sample was heated to 80°C for 10 min instead of being subjected to UV irradiation.

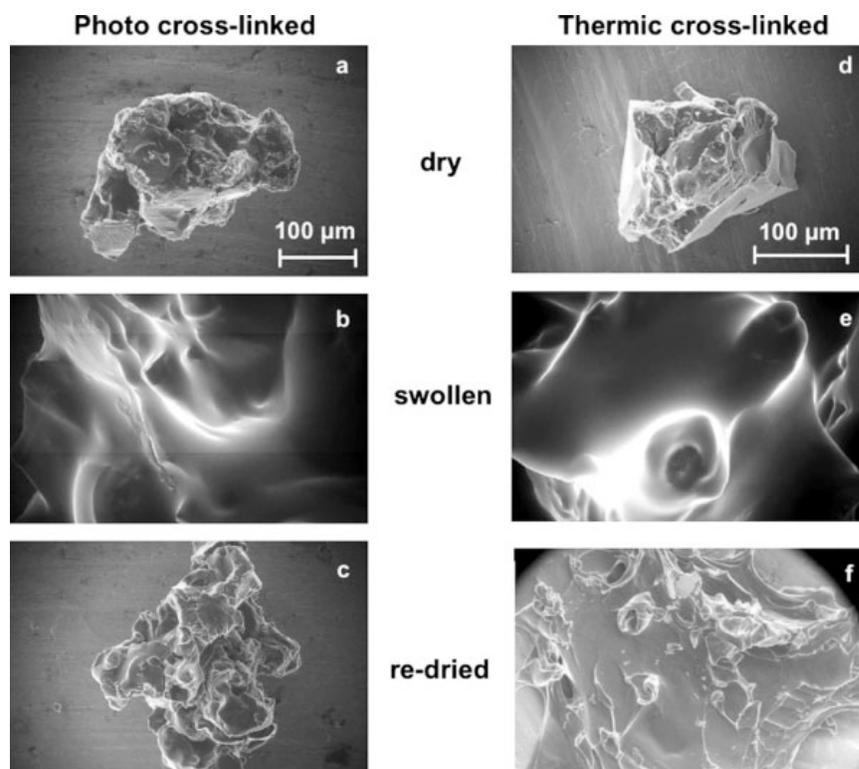


Figure 1 ESEM of the (a–c) photocrosslinked and (d–f) thermally crosslinked superabsorbent particles (a,d) before and (b,e) after swelling with aqueous NaCl solution (0.9% w/w). (c,f) Afterward, the swollen particles were dried *in vacuo* at 2 Torr.

absorbance capacity (CRC and AUL). However, the flow conductivity (SFC) was affected. Under our experimental conditions, the highest SFC was achieved with 5% $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and an irradiation time of 10 min (Table II, Sample 3).

Because an increase in the flow conductivity was observed with the addition of a small amount of HCl (Table I), different counter ions for peroxydisulfate were tested with different acid–base properties. Aqueous solutions of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ are slightly acidic, whereas $\text{Na}_2\text{S}_2\text{O}_8$ solutions are almost neutral. However, no differences in the CRC, AUL, or SFC values were observed (Table II, samples 3 and 5).

Peroxydisulfates are known to cleave thermally to generate radicals, as shown in eq. (1).¹⁷ To show that the surface crosslinking is initiated photochemically and not thermally, a polymer sample coated with a peroxydisulfate solution identical to sample 3 (Table II) was heated for 10 min to 80°C without irradiation. From the values of CRC, AUL, and SFC, which were nearly identical to those of the untreated polymer particles (Table II, samples 1 and 6), it was concluded that no significant surface crosslinking occurred.

A further successful attempt to improve the performance of the photochemically surface-crosslinked

particles was made by the addition of a small amount (0.5% w/w) of PEG-OMe to the peroxydisulfate solution, which was used to coat the particles before irradiation. PEG-OMe is a commonly used dispersion agent for surface coatings. A high flow conductivity was achieved (SFC = 85) while high salt solution absorbance capacities (CRC and AUL) were maintained (Table II, sample 7). The reason for the evidently higher degree of surface crosslinking in the photochemical reaction in the presence of PEG-OMe is not fully understood. We propose that the additive acts as a dispersion agent to improve the uniformity during the coating process. Further spectroscopic investigations are in progress, including laser flash photolysis and electron paramagnetic resonance, to study the role of PEG-OMe in the photochemical crosslinking.

Environmental scanning electron microscopy (ESEM) was employed to study the surface properties of the crosslinked particles. Figure 1(a,d) shows the images of typical particles that were photochemically or thermally crosslinked, respectively. Upon increase of moisture in the ESEM chamber the particles swelled to a size several times their original size [Fig. 1(b,e); only parts of the particles are shown

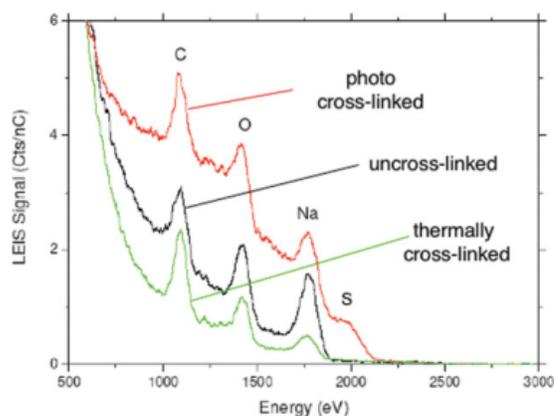


Figure 2 LEIS spectra of the untreated and surface-cross-linked superabsorbent particles.

because of their large size]. After redrying at a reduced pressure (~ 2 Torr) for 30 min inside the ESEM chamber, the photochemically surface-cross-linked particle recovered to its original size [Fig. 1(c)]. However, the thermally surface-crosslinked particle showed major damage and a fractured surface [Fig. 1(f)]. This shows that photocrosslinking produces a more flexible and robust shell on the particles than thermal crosslinking.

Low-energy ion scattering (LEIS) was performed to examine differences in the surface compositions of the crosslinked (photochemically and thermally) and uncrosslinked superabsorbent particles. For the LEIS study, a beam of He^+ ions was used to probe the surfaces. Because of the high probability of neutralization of the ions that penetrate the first atomic plane, LEIS has the characteristic of being sensitive only to the outermost atomic layer of a surface.^{18,19} Figure 2 shows the energy spectrum of the scattered He^+ for photochemically, thermally, and uncrosslinked superabsorbent particles. The peaks are indicative of the atomic composition of the outer surface layer. As expected, the uncrosslinked surface was composed of carbon, oxygen (from carboxylic acid), and sodium (counter ions to carboxylic acid). The thermally crosslinked particles showed the same atoms (C, O, and Na) but with different intensity ratios. A change in the ratio between the atomic peak intensities is a direct indication of surface modification. Table III lists the absolute peak areas (C, O, and Na) and the peak area ratio for C/O. The increased C content, increased C/O ratio, and decreased Na content were probably caused by the added diol ester bridges (Scheme 2) in the thermally surface-crosslinked particles, which buried some of the sodium carboxylate groups.

The photochemically surface-crosslinked particles showed an additional LEIS peak, which was

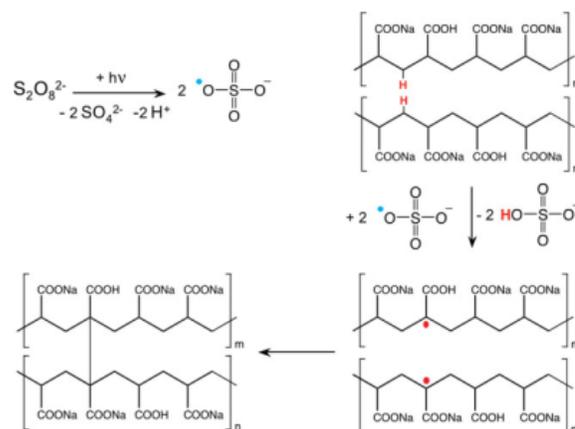
Surface crosslinking	C (counts/nC) ^a	O (counts/nC) ^a	Na (counts/nC) ^a	C/O ^b
None	101	126	124	0.8
Thermal	116	61	13	1.9
UV	117	90	59	1.2

^a Counts/nC = counts per nano-Coulomb.

^b Ratio between the peak areas for C and O.

assigned to sulfur (Fig. 2) and could be ascribed to the decomposition products of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ [eqs. (1) and (2)]. In addition, an increase in the carbon content was observed for thermally and photochemically crosslinked particles versus the uncrosslinked particles (Table III), which probably was caused by increased density of the surface due to the crosslinking. The small decrease in the O and Na content (Table III) could have been caused by decarboxylation on the surface due to direct excitation of carboxylic acid groups. Under the irradiation conditions (200–300 nm) employed, some direct excitation of carboxylic acid could occur and cause decarboxylation under the release of CO_2 .^{20,21}

The multitechnique AUL, SFC, ESEM, and LEIS studies indicate that partly neutralized poly(acrylic acid) particles are efficiently crosslinked on the surface with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as a photoactivated crosslinking agent. Scheme 3 illustrates the proposed crosslinking mechanism. Radical anions ($\text{SO}_4^{\cdot-}$) are generated upon the photolysis of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, which is adsorbed on the particle surface. The generated radical anions abstract hydrogen from the backbone of the poly(acrylic acid) chains. The hydrogen in the α position to the carboxylic acid has the highest



Scheme 3 Schematic of the proposed photoinduced surface crosslinking of the poly(acrylic acid) particles.

probability to be abstracted because it is expected that the resulting carbon-centered tertiary radical will be more stable than the carbon radical in the β position (secondary radical).^{14,22} However, it is known that the rate and position of the hydrogen abstraction from poly(acrylic acid) is sensitive to the pH.^{23,24} In addition, interconversion between the radicals in the β and α positions has been reported.^{23,24} In the photolysis process, it is expected that a relatively high local concentration of polymer radicals will be generated. Two carbon-centered radicals can recombine and crosslink two poly(acrylic acid) chains (Scheme 3). To investigate the hydrogen abstraction and crosslinking mechanism in detail, laser flash photolysis and electron spin resonance experiments are in progress and will be the subject of an upcoming publication.

CONCLUSIONS

Partly neutralized poly(acrylic acid) particles have been successfully surface-crosslinked by UV irradiation with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as a photoactivated crosslinking agent. The proposed crosslinking mechanism involves hydrogen abstraction by the radical anions ($\text{SO}_4^{\bullet-}$) on the poly(acrylic acid) backbone to form carbon-centered polymer radicals, which recombine with one another to bridge the poly(acrylic acid) chains on the surface of the particle. The photochemically surface-crosslinked particles display properties superior to those of the thermally surface-crosslinked particles. Higher AUL and SFC values have been observed. In addition, photochemically surface-crosslinked particles show a more flexible and robust shell, which does not break after redrying of swollen particles. Because the photochemical process is faster (~ 10 min under our experimental conditions) and uses less energy (room temperature) in comparison with the currently used thermal process, this new photoinduced crosslinking process should be very attractive for cost-efficient production of high-quality absorbent materials.

EXPERIMENTAL

Materials

$(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Wako Pure Chemical Industries, Ltd., Osaka, Japan), partly neutralized poly(acrylic acid) particles²⁵ (Nippon Shokubai Co., Ltd., Himeji, Japan), thermally surface-crosslinked superabsorbent particles¹⁰ (Nippon Shokubai), and PEG-OME (Sigma-Aldrich, Inc., St. Louis, MO) were used as received.

Methods

Photochemical surface crosslinking

In a 500-mL separable quartz flask, 10 g of partly neutralized poly(acrylic acid) particles were stirred rigorously with stirring vanes, and 1.05 g of an aqueous $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution (23.8 wt %) was added to the stirred polymer particles. The particles were continuously stirred for 10 min to ensure a homogeneous coating of the particle surfaces with the peroxodisulfate solution. The particles were irradiated under stirring for 10 min with a UV lamp system (UV152/IMNSC3-AA06, Ushio Denki K.K., Tokyo, Japan), which contained a metal halide lamp (UVL-1500M2-N1, Ushio Denki). The UV light intensity at the sample flask was approximately 60 mW/cm^2 .

CRC

The superabsorbent particles (200 mg) were placed uniformly into an $85 \text{ mm} \times 60 \text{ mm}$ nonwoven fabric bag (Heatlon Paper Type GSP-22, Nangoku Pulp Kogyo K.K., Kochi, Japan). The heat-sealed bag was immersed in a 500-mL aqueous NaCl solution (0.9% w/w) for 30 min. The bag was then removed from the solution and centrifuged for 3 min with an H-122 centrifuge (Kokusansha K.K., Tokyo, Japan) with a centrifugal force of 250g. The weight of the bag containing the swollen particles was determined. To correct for the weight of the empty bag, an empty bag (without superabsorbent particles) was treated in the same way, and the mass was subtracted from the weight of the bag containing the swollen superabsorbent particles. The total water absorbance capacity (CRC) was calculated as follows:

$$\text{CRC} = \frac{[(\text{Weight of the bag with swollen superabsorbent particles}) - (\text{Weight of the empty bag})]}{(\text{Weight of the dry superabsorbent particles}) - 1}$$

AUL of 0.7 psi

In the apparatus illustrated in Figure 3, a 400-mesh stainless steel gauze (aperture = $38 \mu\text{m}$) was fused

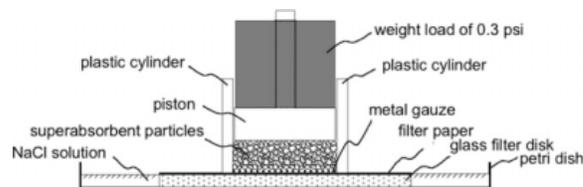


Figure 3 Apparatus used to measure the value of AUL.

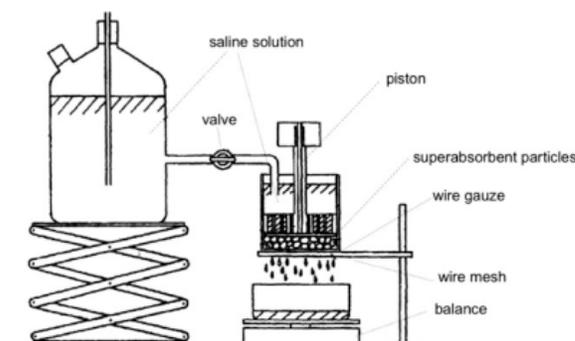


Figure 4 Apparatus used to measure the value of SFC.

to the bottom of a plastic support cylinder (inside diameter = 60 mm). The superabsorbent particles (0.9 g) were distributed uniformly on the gauze. A piston and a weight load were adjusted to supply a pressure of 4.83 kPa (0.7 psi) on the superabsorbent particles. This entire assembly containing the superabsorbent particles was weighed (W_1).

The lower part of the apparatus consisted of a Petri dish (diameter = 150 mm), which contained a glass filter disk (diameter = 90 mm, pore diameter = 100–120 μm ; Sogo Rikagaku Glass Seisakusho K.K., Kyoto, Japan). The Petri dish was filled with an aqueous NaCl solution (0.9% w/w) to the level of the upper surface of the glass filter disk. JIS P 3801 (no. 2) filter paper (diameter = 90 mm, thickness = 0.26 mm, retention particle diameter = 5 μm ; Advantec Toyo K.K., Tokyo, Japan) was placed on top of the soaked glass filter disk so that the filter paper was completely wetted. Any excess liquid was removed.

The upper part of the apparatus, which contained the superabsorbent polymer, was placed on the wetted filter paper of the lower part of the apparatus (Fig. 3). After 1 h, the upper part of the apparatus (containing the swollen superabsorbent particles) was weighed again (W_2), and the AUL value was calculated as follows:

$$\text{AUL} = (W_2 - W_1)/0.9 \text{ g}$$

SFC

Figure 4 shows the apparatus that was used to measure the SFC. The superabsorbent particles (0.9 g) were placed evenly on a stainless steel wire gauze (mesh size = 38 μm), which functioned as the bottom of a cylindrical container (inside diameter = 6 cm). A glass filter plate was placed on top of the superabsorbent particles; it had good permeability for the aqueous saline solution but was impenetrable for the superabsorbent particles. A piston with holes

for water penetration supplied a constant pressure of 0.3 psi to the superabsorbent particles. This assembly rested on a wire mesh, which permitted liquids to pass. The dripping liquid, which was collected in a pan of a balance, which was connected to a computer for data acquisition. For the flow conductivity experiments, a mixture of salts selected to simulate a urine solution was used, and it contained 0.25% (w/w) $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.5% (w/w) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 2% (w/w) NaSO_4 , 0.85% (w/w) $\text{NH}_4\text{H}_2\text{PO}_4$, and 0.15% (w/w) $(\text{NH}_4)_2\text{HPO}_4$ in purified water. This artificial urine mimic was supplied from a tank via a pipe with a valve to the container that contained the superabsorbent particles. The flow from the supply tank was adjusted so that a constant height of the artificial urine from the wire gauze of 5 cm was ensured. The amount of liquid that passed through the gel layer was recorded by the computer-controlled balance over a period of 10 min. The flow speed at time zero [Flow_0 (g of solution/s)] was calculated by extrapolation of the flow during a period of 10 min to Flow_0 with the least-square method. From Flow_0 , the SFC value was calculated as follows:

$$\text{SFC} = (\text{Flow}_0 \times \text{LO})/(\rho \times A \times \Delta P)$$

where LO is the height of the gel layer (cm), ρ is the density of the artificial urine solution ($\rho = 1.003 \text{ g/cm}^3$), A is the area of the gel layer in the 6-cm container ($A = 28.27 \text{ cm}^2$), and ΔP is the hydrostatic pressure on the gel layer (4920 dyn/cm^2). The unit of the SFC value is $10^{-7} \text{ cm}^3 \text{ s/g}$.

ESEM

An XL 30 field emission gun manufactured by FEI (Hillsboro, OR) was used to examine differences in surface swelling/shell recovery among different sets of thermally and UV surface-crosslinked superabsorbent particles by wet/dry/wet cycles in its chamber. Small single superabsorbent particles were placed on the stub of the Peltier cooling stage, which had been mounted into the ESEM chamber before. The relative humidity was adjusted by an increase in the pressure in the chamber from 2 to 7 Torr and by the Peltier stage being kept at 5°C. The hydration/dehydration steps of the selected superabsorbent particles were detected with an environmental secondary discharge detector with a pressure-limiting aperture of 500 μm . Single swelling steps were pictured at increasing pressure steps of 0.5 Torr each from 2 Torr up to saturation, at which the formation of water droplets was visualized. At saturation, smaller decreasing pressure steps of 0.1 Torr were taken to visualize the complete swelling of the superabsorbent sample and the water submerging it. The dehydration steps were captured at 0.5 Torr up

to 2 Torr. The final dehydration state was then achieved by the superabsorbent sample being left at a pressure of 2 Torr, and the final image was taken after 30 min.

LEIS

The surface-crosslinked and uncrosslinked particles were pressed into tablets with a pressure of 150 MPa for 30 s. The tablets were placed into the LEIS chamber, which was evacuated to a pressure of 10^{-9} Torr, and bombarded with He^+ ions at 3000 eV.

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