Deswelling Stresses and Reduced Swelling of Superabsorbent Polymer in Composites of Fiber and Superabsorbent Polymers

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ABSTRACT: The desired performance characteristics of absorbent products such as diapers include a low number of leaks, adequate liquid absorption capacity, and high skin dryness. By measuring the absorption behavior of mixtures of cellulose fluff pulp and superabsorbent polymers in non-immersed conditions, we identify four major parameters that affect the swelling of the polymer in a composite: the Donnan ion-exclusion effects of limiting the amount of liquid in contact with the superabsorbent polymer, the restriction of swelling by the physical constraints of the fibrous network that surrounds the polymer particles, the restriction of swelling by the capillary tension provided by the pores between the cellulose fibers, and the osmotic pressure of extracted polyelectrolytes. Swelling of the superabsorbent polymer in composites is always smaller than the value measured by immersion of the polymer followed by centrifugation. Donnan exclusion of ions from the gel phase results in about 16% less swelling than when the polymers are swollen in excess liquid. The swelling restriction imposed by the fiber network, which surrounds the granules, reduces swelling a further 10%. In addition, the presence of small pores between the fibers exerts capillary tension on the polymer and lowers the swelling by another 10%. The external compression of the composite pads does not reduce the extent of swelling of the superabsorbent polymer because the stress is supported by the fibers. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2493–2507, 2005

Key words: gels; hydrogels; modulus; networks; swelling

INTRODUCTION

Superabsorbent polymers have been in general use in personal hygiene products for just over 20 years. These crosslinked polyelectrolytes absorb aqueous liquids, such as urine, and form a dry, soft, rubbery gel that retains the liquid under moderate pressures. Superabsorbent polymers are the principal reason that absorbent products, such as diapers, can be so thin yet absorbent. Superabsorbent polymers provide two major benefits to these products, dryness and thinness, so that the diapers can be designed to fit better, with reduced leakage.

The absorbent cores of personal hygiene products such as diapers are a mixture of superabsorbent polymer granules, fibrous absorbents such as cellulose, and binders. The purpose of the absorbent core is to take in and absorb urine and prevent the leakage of liquid from the core under body loads. The core is supposed to keep the baby dry.

The two main components, superabsorbent granules and absorbent fiber, provide two ways for liquid to be stored in the absorbent core: trapped within the gel and within the open pores between fibers. Before superabsorbent polymers, all liquid was held in absorbent cores by the pores between fibers by means of capillary forces. In contrast to fibers, superabsorbent polymers function as osmotic absorbents. Water diffuses into dry, crosslinked polyelectrolytes in order to solvate the polymer chains and the counterions. The extent of diffusion is limited by the elastic stress caused by the stretching polymer chains and by any other stresses that act on the polymer phase. Many studies have shown how polyelectrolyte gels respond to various stresses. The effect of salt solutions of different concentrations[1–3] and that of uniform hydrostatic pressure[4,5] are well known where large salt solution baths are used for the studies. The deswelling effect of polyelectrolyte solutions has also been elucidated.[6]

Any stress acting on the superabsorbent polymer results in a change to the swelling ratio. Added stresses on the polymer phase cause deswelling (from a more highly swollen state in the absence of stress) or limit the swelling (from a less swollen state). When different responses to stress are observed between the absorption from the dry state and deswelling from the wet state, it is generally due to differences in the kinetic response of the polymer in absorption and desorption; true equilibrium has not been reached. It

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is known that polyelectrolyte gels deswell slower than they swell.[7]

In an important paper by Horkay and Zrinyi,[8] the application of stress through mechanical anisotropic deformation (uniaxial compression) resulted in equivalent deswelling to an equal magnitude stress applied isotropically by means of an external osmotic stress. The implication of this finding is that all equal magnitude stresses cause equal magnitude deswelling of a given superabsorbent polymer. However, what is the total stress on the superabsorbent polymer in a swollen absorbent core? Based on the findings of Horkay and Zrinyi,[8] the total stress causing deswelling of superabsorbent polymers can be measured by determining the equilibrium swelling degree of a given superabsorbent polymer in a composite pad that is in contact with liquid under realistic conditions.

The choice of realistic conditions complicates the full understanding of superabsorbent polymers in absorbent cores. Most measurements of the absorption of liquid by superabsorbent polymers are done with essentially infinite baths of saline solutions. However, infinite baths of aqueous solutions are essentially never encountered in the personal care industry because the products are designed to be dry. The stresses in a swollen and dry composite system will be a different type and magnitude than in infinite solution baths. Such stresses may be hydrostatic compression, salt partitioning by the superabsorbent polymer (the Donnan effect), restriction by the network of interspersed fibers, competition for liquid by the small capillaries between fibers, and interparticle friction between the polymer particles and the fibers. Furthermore, the role of body forces in limiting the swelling within a composite pad is not fully understood. Some of these stresses have previously been proposed as important in composites of superabsorbent polymer and fluff.[9] When present, and if of sufficient magnitude, these stresses can affect the absorbent properties of the superabsorbent polymer. However, little has been reported about the magnitude of these stresses in absorbent cores and their effect on the swelling of the polymer that is present. In this article we identify the sources and magnitudes of stress in simple composite structures and determine how these stresses affect the swelling of the superabsorbent component. These questions bear directly on the optimum design of absorbent products that contain a swelling superabsorbent polymer. Because the final state of a diaper is supposed to be dry, we have taken this condition into account and measured the contribution of various stresses to superabsorbent polymer swelling in low saturation conditions, using a sample set of superabsorbent polymers containing a variety of crosslink densities and morphologies, such as surface crosslinked polymers that are commonly used in the personal care industry.

EXPERIMENTAL

Polymer swelling ratio

The saturated, equilibrium swelling ratio (Q_{max}) of the polymer was measured by means of the centrifuged retention capacity test. A 0.2-g sample of the polymer powder is sealed in a liquid-permeable tea bag and immersed in a bath of 0.9 wt % NaCl solution. After swelling to equilibrium, the tea bag is centrifuged to remove liquid held in the interparticle pores. The increase in mass absorbed per gram of dry polymer is calculated from the gravimetric results.[10]

Limited solution tea bag swelling method

In use, superabsorbent polymers in composites such as diapers are rarely swollen in a huge reservoir of liquid. To determine the swelling ratio (Q_L) of the superabsorbent polymer when only a limited amount of liquid is available, we used the following method. We isolated 30–50 mesh cuts of the granular superabsorbent polymer samples and then measured Q_{max}. Then, for each sample, we set up a second pair of bags containing superabsorbent polymer. Each bag was placed into a 3.5-in. diameter Petri dish and then saline solution was added to the bag. The amount of saline solution added equaled the product of the mass of polymer in the bag times the Q_{max} value times the fractional swelling desired, plus 0.35 g of extra saline solution needed to wet the tea bag. The dishes were covered and the bags let stand for 60 min. Then, the matched pair of bags was centrifuged as before and the swelling capacity of the superabsorbent polymer was calculated. The swelling ratio of each polymer was measured with saline volumes equal to fractional swelling of 0.4, 0.6, 0.8, 1.0, and 2.0 times the Q_{max} value.

Absorbency under load

The absorbency under load test measures the swelling of a bed of superabsorbent polymer particles from the dry state in a plastic cylinder while the particles are under a silo or bin load. The absorbency under load of the polymers was measured according to the method described by Kellenberger.[11]

Superabsorbent polymer modulus

The shear modulus (G') of the superabsorbent polymer was measured on packed beds of swollen particles by means of oscillatory rheometry with a cone and plate configuration. In order to measure the modulus at the same swelling ratio as is present in the composites, the swelling ratio (Q_{pad}) of each superabsorbent polymer was determined from swelling experiments in the presence of cellulose fiber as outlined in the

TABLE I
Swelling Ratios and Modulus of Polymers Used in This Work

Sample ID	Preparation source	Q_{max} (g/g)	Shear modulus (dyne/cm²)	Q_L (g/g)	Q_{pad} (g/g)	0.3 psi AUL (g/g)	0.6 psi AUL (g/g)	0.9 psi AUL (g/g)
Drytech 2035 (Dow Chemical)	Commercial	29.2	42000	25.2	20.6	30.4	26.0	16.0
Experimental B	U.S. 5,629,377[a]	38.4	22000	32.2	25.5	11.8	7.7	7.2
Experimental C	U.S. 5,629,377[b]	37.3	39300	31.9	25.3	34.5	29.2	20.6
Drytech 535 (Dow Chemical)	Commercial	29.6	40100	25.1	20.8	26.2	10.7	7.8
Favor 880 (Stockhausen)	Commercial	29.4	31800	25.0	20.8	30.7	27.5	23.5
Favor SXM 7500 (Stockhausen)	Commercial	37.7	30100	32.4	23.2	33.2	16.7	10.4
Aqualic CAW4 (Nippon Shokubai)	Commercial	35.1	26200	29.3	21.5	24.2	12.7	8.7
Experimental H	U.S. 5,629,377[c]	42.8	13700	33.8	23.9	7.7	nd	nd
ASAP 2300 (Chemdal)	Commercial	28.0	41300	23.3	18.2	28.4	26.3	22.8
Sanwet IM 4510 (Hoechst–Celanese)	Commercial	30.7	43800	25.9	19.6	31.7	27.8	22.0
Experimental K	WO 01/45758[d]	22.0	50571	19.2	17.7	25.1	22.0	17.0
Experimental L	WO 01/45758[e]	14.7	90300	12.5	11.7	19.3	nd	nd
XUS 40703.02 (Dow Chemical)	Commercial	27.7	47600	23.6	19.8	28.3	23.5	16.4
Experimental N	WO 01/45758[f]	24.7	40100	20.0	16.6	23.3	17.9	13.2
Experimental O	WO 01/45758[g]	18.1	74600	15.0	12.3	21.0	18.0	17.0
XZ-91060.02 (Dow Chemical)	Commercial	27.4	38200	23.9	19.4	26.4	21.8	18.9
Drytech 2024 (Dow Chemical)	Commercial	27.4	60800	24.4	19.8	26.8	12.2	nd
XUS 40695.00 (Dow Chemical)	Commercial	38.8	28300	34.4	24.9	36.7	29.3	22.8
Experimental S	U.S. 5,629,377[h]	32.6	33500	28.2	20.8	24.5	nd	nd
Experimental T	U.S. 5,629,377[i]	33.0	25200	26.7	19.5	18.4	nd	nd

[a] Resin preparation procedure 1; 4000 ppm Sartomer 9035 crosslinker.
[b] Resin preparation procedure 1, heat treatment procedure 3; 2100 ppm Sartomer 9035, 5250 ppm poly(ethylene glycol)-600.
[c] Resin preparation procedure 1; 2500 ppm Sartomer 9035 crosslinker, 8000 ppm glycerol.
[d] Example 7.
[e] Example 15, except with 10,000 ppm Sartomer 9035, 10,000 ppm glycerol.
[f] Example 9, except using polymer powder from comparative experiment 1.
[g] Example 9, except with 8500 ppm Sartomer 9035, 10,000 ppm glycerol.
[h] Resin preparation procedure 1; 5000 ppm Sartomer 9035 crosslinker.
[i] Resin preparation procedure 1; 5000 ppm Sartomer 9035, 10,000 ppm glycerol, with the addition of 5 wt % low molecular weight soluble poly(acrylic acid) to the monomer solution.

Saturation and blotting technique section. A fresh sample of the superabsorbent polymer was then prepared by adding the amount of 0.9% NaCl solution required by Q_{pad} to a known quantity of the polymer (30–50 mesh particles), letting the polymer absorb the saline solution for 60 min, and then measuring the shear modulus on the packed bed of gel according to our previous description of the technique.[12] The resulting values are tabulated in Table I.

Surface tension effects in gel beds

The effect of reduced surface tension on the swelling of the gels was measured by using the limited solution swelling technique described above, but using saline solution that also contained 0.04% sodium lauryl sulfate surfactant (Duponol ME). The absorbency under load (AUL) was also measured with and without the presence of surfactant under the conditions of a limited solution volume. A standard AUL cell was used for limited solution AUL,[11] but the liquid reservoir was a Petri dish that contained only the amount of saline calculated from the superabsorbent polymer amount and its "normal" 0.3 psi AUL value obtained with an infinite reservoir of saline solution. A 1-in. disk of glass-fiber filter paper was placed into the dry Petri dish and the calculated amount of saline solution was added to form a small puddle on top of the filter disk. An additional 0.25 g of saline was added to the saline puddle to allow extra liquid for wetting of the filter disk. The AUL cell assembly was then placed onto the disk through the puddle. The sample was left to absorb liquid for 60 min, and then the mass of the AUL cell was determined after briefly squeezing and blotting the AUL cell to remove unabsorbed liquid from the interparticle pores. The AUL values were also compared with and without surfactant by means of the standard AUL technique (large reservoir of saline solution).

Extraction of polymer from gels and composites

A sample (1.0000 ± 0.0002 g) was weighed into a 30-mL plastic beaker. A mass of 0.9% NaCl solution

equal to the Q_{max} of the polymer sample was poured into the beaker on top of the sample. The sample and saline solution were mixed with a glass stirring rod and then covered and left to swell for 60 min at room temperature. A 250-mL filtering flask with a 60-mL fritted glass funnel was used to filter the swollen gel. Several paper towels were folded and put into the bottom of the flask to prop up an empty vial for filtrate. The small vial was weighed and then placed into the flask upon the paper towels. The stem of the funnel was inserted through the rubber vacuum seal and into the vial, and then the filtering flask was connected to the water aspirator. The swollen gel slurry was poured into the funnel and vacuum filtered for 5 min. For composites, the swollen pad was folded, put into the funnel, and vacuum filtered for 5 min. During the filtration a piece of 6-in. square latex sheeting was laid over the top of the funnel and allowed to press down onto the gel or composite. This provided even pressure on the sample for filtration. The vial containing the filtrate was then weighed, and the mass of the collected filtrate was determined by the difference from the tare mass. The filtrate was poured into a 50-mL glass beaker. The vial was filled three quarters-full with deionized water, capped, and shaken; then, this rinse water was poured into the glass beaker. This was done 3 times to rinse all of the filtrate from the vial. The beaker then contained approximately 40 mL of solution. Extractable acrylate was measured on this solution according to acid–base titration[13] and the milliliters of $0.1N$ HCl titrant were recorded. A blank of 40 g of 0.9% NaCl solution was also titrated. The blank was subtracted from the sample titrant volume to determine the volume of titrant used for each extract. The quantity of polyacrylate in the filtrate was calculated according to eq. (1):

$$65\% \text{ neutralized PAA (g)} = \frac{V_t N E}{1000} \qquad (1)$$

where V_t is the volume of titrant (mL), N is the normality of the titrant, and E is the carboxyl equivalent weight of the superabsorbent polymer [$E = 86.4$ g/equiv for 65% neutralized poly(acrylic acid)]. The polymer concentration (g polymer/g liquid) in the filtrate was calculated by dividing the mass of polyacrylate determined in eq. (1) by the filtrate mass (g).

The filtrate recovered from each sample is not necessarily the entire amount of unabsorbed liquid present in the sample because some of the gel samples do not filter efficiently. The total amount of unabsorbed liquid was determined from the difference between Q_{max} and Q_L. To determine the total amount of polymer extracted from each gram of dry superabsorbent polymer, the mass of polyacrylate in the filtrate sample obtained in eq. (1) was multiplied by the ratio of the expected total filtrate mass (from the tea bag experiments) to the filtrate mass obtained in the filtration.

Construction of composites

The properties of the composite pad are very sensitive to the gel mass fraction in the pad, because the volume of the superabsorbent polymer dominates the volume of the composite after swelling. Therefore, it is extremely important to know the precise amount of superabsorbent polymer in the test sample. Estimating the amount of superabsorbent polymer in a piece of a composite that has been cut from a larger sample is not accurate enough for good interpretation of the data. For this work, we built a small, vacuum-operated pad former that was capable of directly yielding 3-in. diameter composite disks with exact amounts of cellulose fiber and superabsorbent polymer and no need to trim the final piece. This device enabled us to make composite pads with high reproducibility.

Each 3-in. diameter pad was made with 1.00 g of superabsorbent polymer (30–50 mesh) and 1.00 g of fluff plus a 3-in. diameter tissue on top and bottom. The tissues contributed 0.15 g to the mass of the composite. The superabsorbent polymer was gradually fed into the unit by means of a vibrating feeder. The fluff was gradually added by hand through a small slot and blended with the superabsorbent polymer by means of a small air jet inside the forming chamber. A HEPA vacuum cleaner was used to pull the mixture onto the tissue paper. The pad preparation was done at room temperature and at about 50% relative humidity. The pad was consolidated by pressing the pad for 45 s at 100°C with 1/8-in. shims in a Dake brand heated, hydraulic press. Each pad was weighed after pressing and weighed approximately 2.15 g. After pressing, the pads were stored individually in labeled plastic Petri dishes.

Saturation and blotting technique of pads

To each pad in its Petri dish was added the amount of 0.9% NaCl solution equal to the Q_{max} of the polymer used in that pad multiplied by the mass of the polymer present. The saline solution was spread evenly over the entire area of the pad so that the pad was uniformly wet. The dish was covered and let stand at room temperature for 60 min.

Then, the Petri dish cover was removed momentarily and a stack of four 3-in. blotter disks was placed on top of the wet pad. The cover was replaced and the Petri dish was turned over. The bottom of the dish was then removed and another stack of four 3-in. blotter disks was placed on top of the wet pad. This maneuver yielded a sandwich structure with the wet pad between two stacks of blotter card. The total mass of

blotter card used per pad was about 11 g. Then, a 3.25-in. diameter, 5-kg weight was added on top of the sandwich to compress the blotters against the wet pad. After waiting 5.0 min, the 5-kg weight was removed and the top stack of blotters was carefully lifted off the pad, using a spatula. The lid of the Petri dish was tared and placed on top of the blotted pad. The dish was again turned over, the other stack of blotters was removed, and the blotted pad was weighed. If the stacks of blotter cards were fully saturated after this procedure (determined by visual observation), a new set of dry blotters was positioned around the pad and the blotting was repeated. The total liquid absorbed by the pad was measured gravimetrically. From this value we subtracted 1 g liquid/g cellulose fiber present. The remainder was divided by the mass of the superabsorbent polymer in the pad to obtain Q_{pad}.

Superabsorbent polymer swelling in composites under load

The swelling ratio of the superabsorbent polymers in pads that were under a body load during swelling was measured using the blotting procedure as described above, with a slightly different saturation procedure. The dry pad was placed in a 5.5-in. glass Petri dish. A 3.5-in. glass Petri dish was placed on top of the pad, and a 1- (0.3 psi) or 2-kg (0.6 psi) weight was placed into the upper dish to provide compression on the pad. The requisite amount of saline solution was poured into the larger Petri dish near the edge of the dry pad. When the saline solution made contact with the pad, the liquid wicked into the pad. After the desired swelling time, the weight and upper glass dish were removed and the pad quickly blotted as before.

Surface tension effects

The effect of the capillary tension from the fiber matrix on the swelling of the superabsorbent polymer was studied by comparing the swelling of composites in saline solutions with and without the presence of Duponol ME surfactant. A pair of otherwise identical 3-in. pads was made. To one pad was added 0.9% NaCl solution and to the other pad was added 0.9% NaCl solution also containing 0.04% by weight Duponol ME. The pads were let stand for 60 min in covered Petri dishes and then blotted, and the swelling ratio of the superabsorbent polymer was determined from the wet mass of the pad.

Absorption by composite pads under body load

The absorption and swelling of pads while under a body load was measured using a specially constructed demand absorbency device. A coarse grade, 3.5-in. fritted glass Buchner funnel was modified by cutting off most of the top cylindrical portion so that a rim of only 1.5 cm remained above the surface of the fritted glass surface. This shortened funnel was clamped in a ring stand. The bottom stem of the funnel was connected to the bottom outlet of an aspirator bottle. The aspirator bottle served as the liquid reservoir that supplied the fritted glass surface with a continuous supply of saline solution. The neck of the aspirator bottle was fitted with a rubber stopper containing a single hole that held a length of polyethylene tubing. This section of tubing served as a liquid head level control to assure a constant, 0-cm liquid head relative to the fritted surface. The aspirator bottle was placed on a recording balance to enable measurements of the absorption.

The 3-in. circular composite disks of known mass were placed on the level, fritted glass surface to begin the absorbency measurement. The bottom of a 3.5-in. plastic Petri dish was quickly placed on top of the pad and a 2-kg weight was centered on the Petri dish to provide the compression (0.6 psi) during swelling. The mass loss from the reservoir was recorded and used to calculate the absorbency of the pad per gram of dry pad.

RESULTS AND DISCUSSION

Because the amount of liquid added to absorbent composites is limited in practice, we measured the effects of limited solution volumes on the swelling properties of superabsorbent polymers in composites and determined how the properties of the superabsorbent polymers affect the position of the swelling equilibrium in the presence of cellulose fiber. We now discuss the swelling properties of polymers in the presence of limited saline solution volumes and then discuss gel swelling parameters in composite pads to determine the extra stresses encountered in the presence of fibers.

Polymer sample set

A sample set of 20 superabsorbent polymers was chosen to provide materials from various Dow experimental chemistries and crosslink densities as well as from several commercial competitors. Sample preparation examples and reference sources are given in Table I. The swelling ratios and modulus of the samples are also given in Table I.

Gel swelling: Donnan equilibrium and its effect at limited liquid volumes

Superabsorbent polymers are polyelectrolyte networks. The absorption of salt solutions by the superabsorbent polymer is therefore affected by ion exclusion from the gel. Sodium ions in the unabsorbed liquid (and an equimolar quantity of the chloride co-
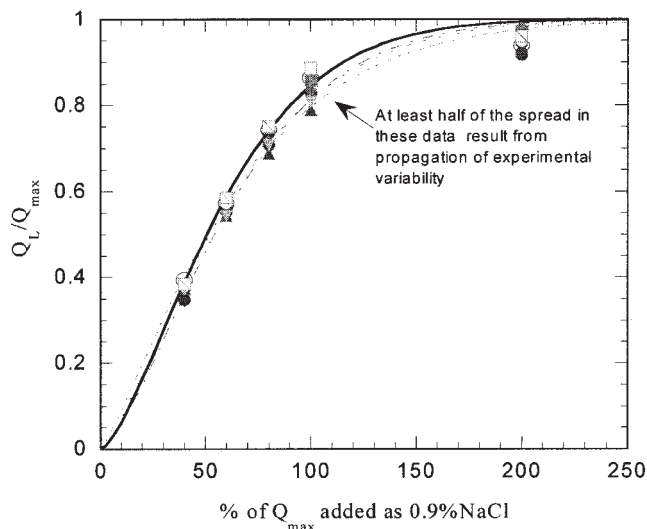
Figure 1 The swelling ratio as a function of the amount of liquid added.

ion) are partially excluded from the polyelectrolyte gel phase at equilibrium so that the activity of sodium ions becomes equal in both phases. Because sodium ions are already present in the gel from its preparation, and because these ions must remain in the gel phase to maintain electroneutrality, some of the sodium ions from the sodium chloride are excluded from the gel phase. Water is thus preferentially absorbed. This phenomenon was first described by Donnan and Guggenheim in 1932 in relation to ionic membranes.[14]

When the salt concentration in the external salt solution is held constant by means of a large excess of the swelling solution that dilutes the excluded salt, the salt exclusion effect can be calculated using the equations of Donnan. For example, a typical sodium-neutralized superabsorbent polymer that is swollen to equilibrium (to 30 g/g) in a large excess of 0.9 wt % NaCl solution will have a NaCl concentration inside the gel phase of approximately half its value in the external phase.[15] However, the original Donnan equations do not account for real values of ion activity coefficients, do not account for elastic stresses present during swelling of ionic networks, and do not accurately describe the process when the amount of external liquid phase is small relative to the gel phase. Then, the salt exclusion results in a change in salt concentration in the external liquid phase. In order to better understand the performance of superabsorbent polymers in real products, where the amount of liquid is indeed limited, we measured the swelling of superabsorbent polymers in various amounts of saline solution and compared the results to the swelling in a large excess of liquid.

The Q_{max} values in Table I were measured in an excess of 0.9% NaCl solution. New samples were

swollen in limited volumes of saline solution to obtain Q_L. Figure 1 plots the Q_L/Q_{max} ratio of each polymer versus the fraction of added liquid (expressed as a percentage of Q_{max}). We observed that all the polymer samples that were tested absorbed limited volumes of liquid in a similar way.

At each liquid addition quantity studied, the polymers swell less than Q_{max}. For example, suppose we swell 1 g of a polymer with $Q_{max} = 30$ g/g. The graph in Figure 1 shows that, when this sample is wetted with only 30 g of saline solution (100% of Q_{max} on the x axis), the sample only swells to about 0.83 of Q_{max} (about 25 g/g). The reduction factor is the same for all the polymers, irrespective of their crosslinking chemistry or crosslinking ratio. The swelling ratio does not reach Q_{max} until the amount of liquid added is greater than twice the saturated, equilibrium swelling ratio value times the mass of the polymer.

The data in Figure 1 can be viewed in a different way by considering each group of data points along the x axis. Each group represents the entire 20-polymer sample set wetted with liquid in the same relative amount (40% of Q_{max}, 60% of Q_{max}, etc.). This is shown in Figure 2. The thickest line represents the hypothetical equivalency of Q_{max} and Q_L. The slopes of each line represent a swelling efficiency at each value of the relative insult amount. The efficiency is highest at the lowest relative insult amount. We also measured the magnitude of this effect on the AUL test. If the quantity of liquid supplied to the AUL cell is limited to some fraction of the AUL value measured with an infinite supply reservoir, the absorbency is lowered just as it is in the tea bag swelling method.
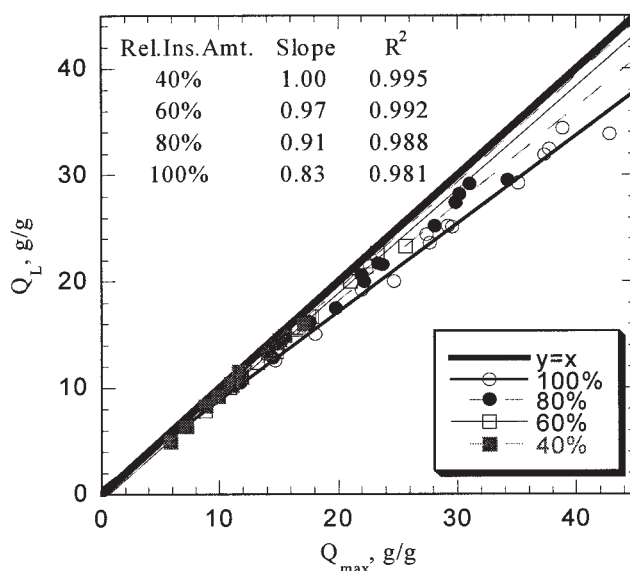

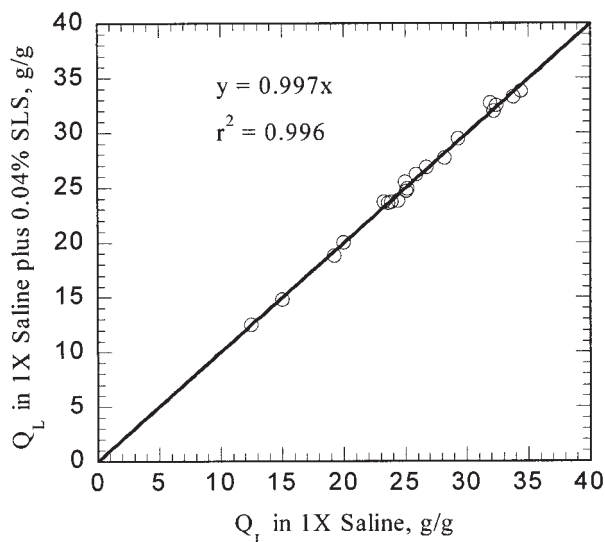**Figure 2** The swelling efficiency of superabsorbent polymers at various insult amounts.

Figure 3 The gel swelling (Q_L) compared to with and without surfactant present.

Gel swelling: Capillary tension effect on gel beds

The swelling of superabsorbent polymers might be affected by capillary tension that may be present in the gel beds as a result of the interparticle pores. We tested for this in the limited solution capacity test and in the AUL test. No effect of capillary tension is possible in the saturated, equilibrium swelling ratio test because the gel bed is immersed in liquid. In limited solution tests, the pores between particles may be sufficiently empty to exert a capillary tension. If a significant capillary tension was present when the swelling was done with standard saline solution, the comparative swelling in surfactant-modified saline solution should yield larger swelling ratios. The results with and without surfactant are compared in Figure 3. In this graph we observe no difference in the swelling between gel beds in either standard saline or saline with surfactant. Either the pores between gel particles are too large to exert a significant capillary tension or the pores are still completely filled with liquid. A similar comparison was made with the AUL test, and again we found no difference in the swelling ratio when using standard saline solution or a saline solution with surfactant. Therefore, the reduced swelling of gel beds in limited amounts of saline solution is not due to capillary tension effects.

Gel swelling: Effect of extractable polymer

Extracted polymer will exert a deswelling stress on the gel phase. The crosslinked polymer concentration in the gel phase will increase because of this stress. The deswelling stress is in the form of osmotic pressure, which is proportional to the polymer concentration.

The osmotic pressure in the original gel phase, which is proportional to the gel phase polymer concentration, will increase when surrounded by a polymer solution. The effect can be estimated by means of eq. (2). For example, a polymer swollen to 30 g saline/g polymer has a polymer concentration of $1/31 = 0.032$ g polymer/g solution (or 3.2% polymer).

If this gel is now surrounded by a solution containing 1% soluble polyacrylate, the gel comes under a pressure equal to the osmotic pressure of the solution, which is proportional to the polymer concentration times the activity coefficient of the polymer.

$$C_{gel} = \frac{1}{(Q_{gel} + 1)} = \frac{1}{(Q_{max} + 1)} + C_{soln}\gamma_{PANa} \quad (2)$$

where Q_{gel} is the resulting swelling ratio of the polymer in the saline polymer solution, C_{gel} is the polymer concentration in the gel phase in the presence of the external polymer solution, C_{soln} is the polymer concentration in the external liquid phase, Q_{max} is the swelling ratio measured in an infinite bath, and $\gamma_{PANa} = 0.33$ is the activity coefficient of sodium polyacrylate in saline solution.[16] For a superabsorbent polymer swollen to 30 g/g in a large excess of 0.9% NaCl solution and being immersed in a saline solution containing 1% soluble sodium polyacrylate, the real swelling ratio would be 27.1 g/g. This is equivalent to a deswelling pressure of about 0.12 psi [see eq. (4)]. For a 40 g/g superabsorbent polymer, the swelling capacity in a 1% solution of polyacrylate (same deswelling pressure) is 35.1 g/g.

Usually, the total amount of soluble polymer, measured by a 16-h extraction, will increase as the saturated, equilibrium swelling ratio increases because of a common link to the crosslink density. The general relationship determined from the 20 samples in this study is shown in Figure 4. The large correlation coefficient indicates that most of the difference in ex-
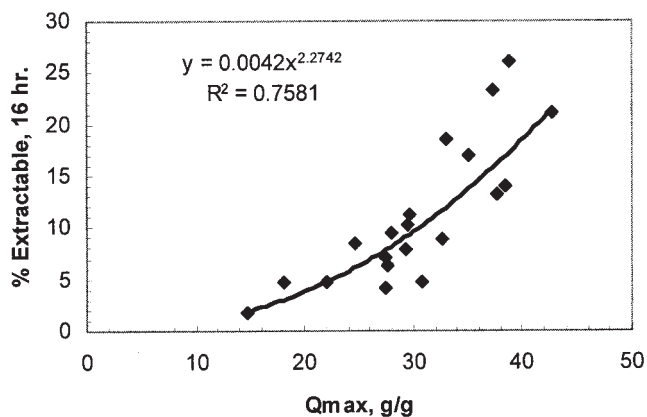

Figure 4 The 16-h extractables versus the saturated, equilibrium swelling ratio of the polymer.

TABLE II
Extractable Polymer Data for Particulate Superabsorbent Polymers

Sample ID	Extractable polymer by 16 h method (wt %)	Extractable polymer by 1 h limited saline method (wt %)	Polymer concn in filtrate (g/g)	Extracted polymer in pad as wt % of total SAP	Polymer concn in pad filtrate (g/g)
Drytech 2035 (Dow Chemical)	7.9	2.1	0.005	2.2	0.0026
Experimental B	14.1	4.9	0.008	5.0	0.0037
Experimental C	23.3	1.5	0.003	1.8	0.0015
Drytech 535 (Dow Chemical)	11.2	5.0	0.011	3.8	0.0044
Favor 880 (Stockhausen)	10.3	1.8	0.004	1.3	0.0015
Favor SXM 7500 (Stockhausen)	13.3	2.5	0.005	2.6	0.0018
Aqualic CAW4 (Nippon Shokubai)	17	5.9	0.010	4.3	0.0032
Experimental H	21.2	9.2	0.010	8.1	0.0043
ASAP 2300 (Chemdal)	9.4	2.0	0.004	1.7	0.0017
Sanwet IM 4510 (Hoechst–Celanese)	4.7	1.2	0.002	0.9	0.0009
Experimental K	4.8	2.2	0.008	2.0	0.0047
Experimental L	1.7	0.7	0.003	0.7	0.0023
XUS 40703.02 (Dow Chemical)	6.3	2.8	0.007	2.0	0.0025
Experimental N	8.5	4.6	0.010	3.6	0.0045
Experimental O	4.7	2.0	0.006	2.7	0.0047
XZ-91060.02 (Dow Chemical)	7.1	2.1	0.006	1.8	0.0023
Drytech 2024 (Dow Chemical)	4.1	2.4	0.008	1.8	0.0024
XUS 40695.00 (Dow Chemical)	18.2	1.6	0.004	2.1	0.0015
Experimental S	8.8	4.1	0.009	3.7	0.0032
Experimental T	18.5	6.0	0.010	8.9	0.0066

tractable polymer content between samples is therefore attributable to differences in the crosslink density. The scatter in the data from the curve indicates the part of the total extractable polymer not related to differences in the crosslink density. The link between the extractable polymer and crosslink density suggests that superabsorbent polymers with larger Q_{max} may have larger possible deswelling than materials with smaller Q_{max}. The concentration of polymer in each of the filtrates from polymer-only extractions (as distinct from extractions from composite) is shown in Table II. Also shown are the values of the total polymer amount extracted in this procedure as a percentage of the dry polymer mass. The amount of polymer extracted in 1 h by a limited volume of saline solution is only a fraction of the total amount extractable in 16 h in excess saline, and a separate relationship emerges for polymers with surface crosslinked morphologies. The relationships are visualized in Figure 5. For the nonsurface crosslinked polymers, about 39% of the total extractable polymer extracts into the limited volume of the free liquid phase in 1 h. For the surface crosslinked morphologies, there is no good correlation between the 16-h value and the 1-h extraction with limited liquid volume. The extraction rate is perhaps more controlled by the nature of the crosslink density in the shell of these core–shell particles.

A plot of the polymer *concentration* found in the free liquid phase surrounding each gel sample versus the 16-h extraction value is shown in Figure 6. The figure shows that the polymer concentration does not de-

pend on the total amount of extractable polymer when the superabsorbent polymer is contacted with just 1 equiv of saline solution. More polymer mass is extracted from samples with higher total soluble content, but that polymer is diluted by more external liquid phase volume as Q_{max} increases. This is because more saline solution is added to the polymers with larger Q_{max} than to the superabsorbent polymers with lower Q_{max} when each is insulted with "1 equiv." Therefore, we found that the concentration of polymer in the external phase (column 5, Table II) remained roughly near 0.7 wt %. The nonsurface crosslinked samples tend to have higher concentrations and the surface crosslinked samples tend to have lower con-
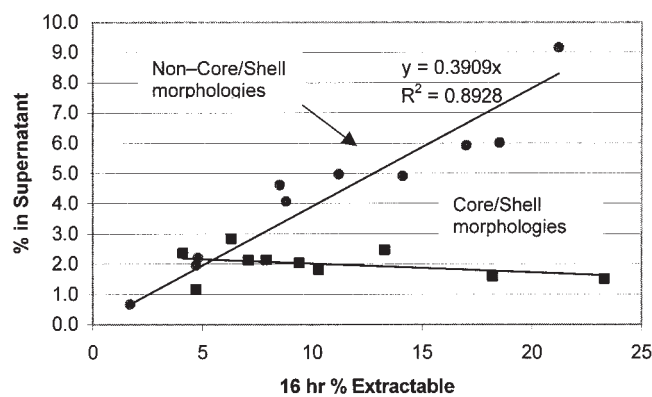

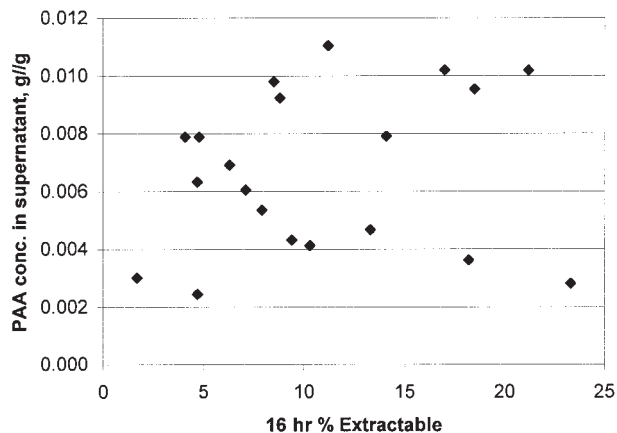**Figure 5** The extractables in 1 h with limited liquid versus 16-h extraction.

Figure 6 The polymer concentration in liquid surrounding gel versus the 16-h extractable value.

centrations from this rough value. This feature helps explain why differences in the extractable polymer have not been well correlated to pad performance.[17]

Composite swelling: Capillary tension

When the fibrous network of a composite pad is not fully saturated, a capillary tension exists that acts to draw liquid into the pore spaces between the fibers. The magnitude of this capillary tension depends on the size of the pores, the surface tension of the liquid, and the wetting properties of the solid. The relationship is given by the Laplace relationship, eq. (3),

$$P_c = \frac{2\sigma\cos\theta}{r_c} \qquad (3)$$

which evaluates the capillary tension (P_c) in terms of the surface tension (σ) at the air–liquid interface, the contact angle (θ) of the liquid on the solid, and the radius of the capillary (r_c). For a porous medium that contains a distribution of pore sizes, like a cellulose fluff pad, a distribution of capillary tensions exists alongside a distribution of the number of pores at each pore volume. The coupling of the distributions of pore sizes and volumes gives rise to an empirical capillary tension–saturation relationship for the porous medium. Small pores exert a high capillary tension and therefore have a large driving force to pull liquid into the pores. However, a small pore has a small volume, so that the volume of liquid trapped within the pore is small. The total volume of each pore size in the structure relative to the total pore volume, along with its specific capillary tension, defines one point on the capillary tension–saturation curve. Some of the capillaries in typical pads of cellulose fluff have sufficient capillary tension to compete for liquid with superab-

sorbent polymer particles for the liquid present in the composite structure.

This deswelling tension may be determined from the difference of the gel swelling in the composite with and without the capillary tension present. We achieve this experimentally by swelling polymers in the presence or absence of a surfactant. The surfactant method works by lowering the surface tension of the swelling liquid, thereby reducing the capillary tension according to the Laplace equation. Because surfactants cannot lower the surface tension of water to zero, the capillary tension cannot be reduced to zero by this method.

The swelling of each of the superabsorbent polymers was evaluated in pads with and without surfactant. From the Laplace equation we can estimate the magnitude of the capillary tension difference expected between the two swelling conditions. The difference in surface tension between the water and the surfactant solution is about 48 dyn/cm. The contact angle of water on prewet fluff is taken as zero. In addition, the average capillary radius in the wet fluff is about 150 μm.[18] Using these data and eq. (4), the capillary tension difference is calculated to be 0.64 kPa (0.093 psi). The ratio of the swelling ratio without surfactant Q_{pad} to the value with surfactant $Q_{pad,SLS}$ is proportional to the capillary tension difference in the pores according to eq. (4),

$$\frac{Q_{pad}}{Q_{pad,SLS}} = \left(1 + \frac{\Delta P_c}{G_{SLS}}\right)^{-0.44} \qquad (4)$$

where G_{SLS} is the shear modulus of the gel at the ratio of swelling $Q_{pad,SLS}$. This equation was previously derived to account for the swelling changes in superabsorbent polymer gels under a hydrostatic pressure (or any other uniform compression such as the capillary tension in the present case).[19]

When the G_{SLS} of the polymer is large, corresponding generally to a small Q_{max}, or to an incompletely swollen polymer, a given value of the capillary tension difference will have a relatively small effect on the swelling ratio. As the shear modulus decreases in concert with an increase in Q_{max}, the capillary tension will have an increasing negative impact on the real gel swelling in the composite. For example, the NSKK sample in Table I has a G_{SLS} value equal to 2.6 kPa, from which we estimate the value of $Q_{pad}/Q_{pad,SLS}$ = 0.91. In other words, the swelling ratio in surfactant solution should be about 10% larger than the value in the absence of surfactant.

The experimental results are shown in Figure 7. The swelling ratio Q_{pad} of each superabsorbent polymer in saline solution while within the fibrous structure is plotted versus Q_{max}. The two sets of data show the behavior of the superabsorbent polymer in solutions
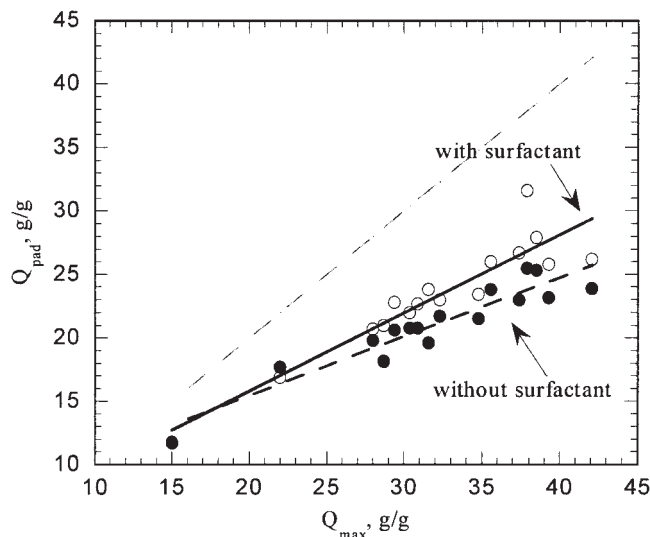
Figure 7 The swelling of superabsorbent polymers in composites with and without surfactant.

with and without surfactant present in the swelling liquid. Least-squares line fits have been calculated and are shown on the graph. The polymers swollen in the presence of surfactant absorb more liquid than when swollen in the absence of surfactant. The differences between the lines are larger at higher Q_{max} (lower modulus), as predicted. The ratio of swelling at Q_{max} = 35 g/g (the same NSKK sample) is 0.90, compared to the earlier estimated value of 0.91.

Composites swelling: Fiber network

In order for the superabsorbent polymer to swell to its maximum possible value, the fibers of the cellulose fluff must be pushed apart to some degree. Therefore, the fiber "network" resists swelling. It was this phenomenon that was originally proposed as the rationale for superabsorbent polymers with higher AUL. The first step in measuring the contribution of this deswelling stress was to measure the effect of the dry compression of the fibers on gel swelling.

Because the dry-compression step of pad forming is a possible source of variability in the pads, we measured the swelling ratio of one superabsorbent polymer (experimental B sample, Table I) in pads with a constant amount of fluff, but compressed to different dry thickness. This yielded pads with different dry densities but equal compositions. Although the dry densities of the pads varied from 0.066 to 0.385 g/cm^3, the swelling ratio of the polymer remained constant at 25.6 ± 0.22 g/g.

We further evaluated the effect of the dry fluff density on the wet fluff density (absent of any polymer). The resulting data in Table III show that the wet density of the fluff reaches a constant value of 0.063 g/cm^3 when the fluff is fully saturated by saline solution, irrespective of its dry density. For composite pads consolidated by dry pressing, we did not observe any effect on the gel swelling caused by differences in the density of the fiber network. Any reduction in gel swelling in the presence of fiber must therefore be due only to the number density of fibers in the swollen pad.

In order to measure the magnitude of the restriction in the absence of the effects of salt concentration and residual capillary tension, the pads were swollen in a large excess of saline solution. Pads were made with different mass ratios of fluff and superabsorbent polymer to yield pads with different gel volume fractions after swelling. After swelling the pads for 60 min in at least a threefold excess of saline solution (based on Q_{max} and mass of the superabsorbent polymer) the excess liquid was drained and then blotted from the pads in order to measure the swelling ratio of the superabsorbent polymer. The deviation of this value from Q_{max} (no fiber restraint) was used to calculate the hydrostatic pressure applied by the fiber network at different gel volume fractions in the composite, by means of eq. (4). The results shown in Figure 8 were fit with a percolation theory model according to eq. (5),

$$P = P_0(f - f_c)^b \qquad (5)$$

The equivalent deswelling pressure (P) is fit in terms of the maximum pressure (P_0); the wet fiber mass

TABLE III
Dependence of Wet Density of Fluff-Only on Dry Thickness

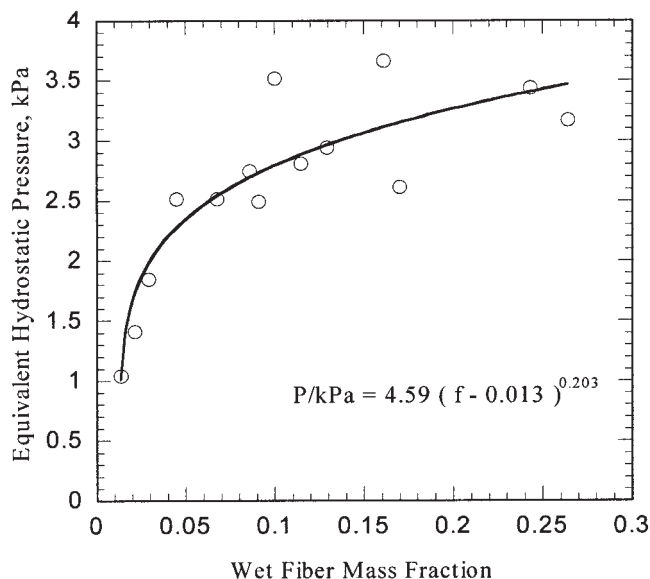| Shim (in.)	Dry mass (g)	Dry thickness (in.)	Wet thickness (in.)	Wet fiber density (g/cm^3)
1/32	1.69	0.023	0.207	0.062
1/16	1.69	0.056	0.198	0.064
3/32	1.67	0.136	0.192	0.066
1/8	1.66	0.180	0.198	0.063
5/32	1.68	0.218	0.205	0.062
3/16	1.63	0.274	0.205	0.060
7/32	1.68	0.293	0.207	0.061
	Average = 1.67 ± 0.02			Average = 0.063 ± 0.002

Figure 8 The equivalent pressure exerted by fiber as a function of the volume fraction of fiber in the wet state.

$$P/kPa = 4.59\,(\,f - 0.013\,)^{0.203}$$

fraction (f); a critical mass fraction (f_c) below which the fiber exerts no equivalent hydrostatic pressure; and the critical exponent b, which is related to the dimensionality of the space in which the percolation process operates. During swelling, the fraction of fiber in the pad decreases as the polymer gel increases in volume, so that the pressure exerted by the fiber is greatest at a low swelling ratio and decreases as the polymer continues to absorb water. The fit parameter $f_c = 0.013$ is interpreted as the smallest fraction of fiber that yields a continuous path through the gel (1.3%).

The fit parameter $P_0 = 4.59$ means that the maximum pressure exerted by the wet fiber, at the limit of 100% fiber, would be 4.59 kPa or 0.67 psi. The best-fit critical exponent $b = 0.203$ is between the theoretical values[20] for two dimensions ($b = 0.139$) and three dimensions ($b = 0.40$), suggesting that the swelling of the flat, composite disks occurs nonuniformly in the three dimensions of the pad.

Composites swelling: Extractable polymer

Because superabsorbent polymers in pads swell less than the same polymers alone, the amount of polymer extracted from the gel phase in pads may be less than from the polymer particles alone. The extraction of polymer from pads was done in an analogous manner to that of the polymer samples alone, as described in the Experimental section. The results are given in Table II.

The *amounts* of extracted polymer from the gel-only extractions and the pad extractions are compared in Figure 9, from which we see that the amounts from the two different extractions are mostly the same. How-

ever, the *concentrations* of the extracted polymer are not the same and it is the concentration of polymer in the external liquid phase that affects the swelling ratio. We found that the concentration of extractable polymer in the pads is about half the concentration in the gel beds. Because the swelling ratio of superabsorbent polymers is less in pads compared to gel beds alone, the soluble polymer present is more dilute in the pads and will exert a proportionately smaller deswelling effect. For the $Q_{max} = 30$ g/g polymer example given earlier, contact with a 1% polyacrylate solution resulted in a swelling ratio of 27.1 g/g. This same polymer will swell less in the composite, leaving more unabsorbed liquid; hence, the extracted polymer will be diluted more. In this example, the polyacrylate concentration would be diluted to 0.5% and the swelling reduction due to extractable polymer is halved, yielding a swelling ratio of 28.5 g/g.

In addition to the deswelling effect caused by the extractable polymer in the unabsorbed liquid phase, another source of inefficiency in superabsorbent polymer absorbency is implied by these findings. The saturated, equilibrium swelling ratio value, from which diaper absorbency is calculated, is measured from a large excess volume of saline solution. The polymer fraction that extracts does not contribute to the absorbency value measured by the centrifuge retention capacity, but this source of inefficiency is "corrected for" in the calculation because the numerator of the ratio is the total polymer amount unadjusted for the extractable portion. Two hypothetical yet plausible examples can demonstrate. Sample A has a Q_{max} of 30 g/g and 10% extractable polymer in the standard tests. Sample B also has a Q_{max} of 30 g/g but has 20% extractable polymer. The comparison in Table IV shows the comparative situation.

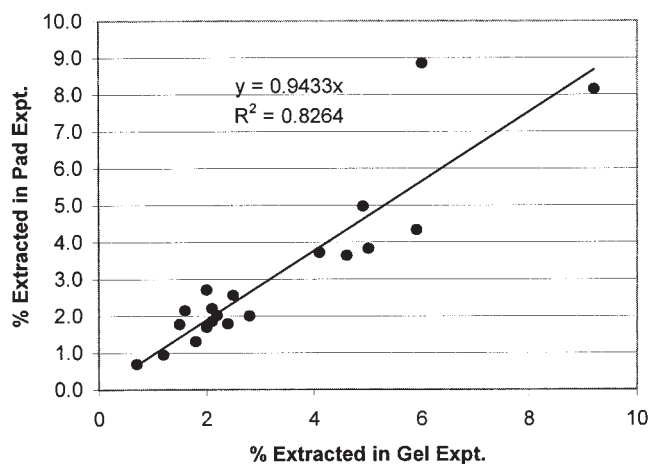The value of total gel phase mass (column 5, Table IV) shows hardly any difference between the samples.

Figure 9 A comparison of the extracted polymer in pad versus gel experiments.

<div align="center">

TABLE IV
Calculating Effect of Extractable Polymer on Product Efficiency

</div>

	Grams saline in gel*	Grams polymer in gel at equilibrium	Grams polymer washed away at equilibrium	Total gel phase mass	True swell ratio of gel	Grams lost capacity by extracted polymer
Eqn.	$m_L = $ CRC m_T	$m_P = 1 - f_X$	$m_X = f_X$	$m_G = m_L + m_P$	$Q = m_L/m_P$	$m_{\text{lost}} = Qm_X$
Sample A	30	0.90	0.1	30.9	33.33	3.33
Sample B	30	0.80	0.2	30.8	37.5	7.50

m_L, mass of liquid absorbed; m_T, total dry SAP mass weighed out; m_P, polymer mass in gel; f_X, the mass fraction of extractables by 16-h test.

Because of different content of extractables, the amount of network polymer doing the work of absorption is different (column 3) and the true swelling ratios (column 6) are different than those estimated by Q_{max}. The true swelling ratios show that sample B has a lower crosslink density than sample A and therefore would have a lower gel modulus, even though the value of Q_{max} is the same. The absorption lost with the extracted polymer is shown in the last column. This amount represents the lost efficiency of liquid absorption due to the noncrosslinked portion. This loss is in addition to the detrimental effect of the osmotic pressure of the polymer solution surrounding the gel. When extraction times are shorter, the loss of polymer from the gel is less than shown in the last column of Table IV, but the differences in crosslink density and resultant modulus are reflected in the swelling ratios shown in column 6.

Composites swelling: Body loads

Another possible stress on the superabsorbent polymer in composites is a body load, for example, provided by an infant sitting on a diaper. To determine the magnitude of this stress, we measured the swelling of the superabsorbent polymer in the pad under load by blotting away the liquid unabsorbed by the superabsorbent polymer. We then compared the values of superabsorbent polymer swelling in pads under load to the values measured in the absence of the fiber. Any specific effect of body load then could be determined after subtracting the osmotic stresses (salt and extractable polymer) and the capillary tension. The values of gel swelling in pads under load at 0-, 0.3-, and 0.6-psi pad compression are shown in Figure 10. The values are plotted with Q_{max} as the x axis so that we can visualize any unusual effects due to crosslink density provided by different processes of superabsorbent polymer manufacturing. For each set of data at the three loads, the least-squares fit line is drawn. The virtual congruence of the lines indicates that the superabsorbent polymers swell the same amount in the pad, regardless of the compression applied to the pad.

The fiber network must be supporting much of the applied load. In this work we find that the lower swelling of superabsorbent polymer in composite pads results from the effects of extractable polymer, capillary tension in interfiber pores, salt concentration, and fiber compression, not body loads.

This finding begs the question What about the pressure dependency observed in the polymer-only AUL test? From the AUL testing in the presence of surfactant, we know that capillary tension does not play a significant role. Because the test uses a large reservoir of liquid, an extra Donnan effect does not play a role. In addition, obviously fiber restriction of the particles does not play a role. Certainly, the extractable polymer affects the results. Therefore, most of the deswelling stresses present in a composite pad are not present in the AUL test. Therefore, it seems possible that the load applied by the piston and weight could substitute for the sum of stresses present in a pad. If so, then at least one of the AUL values should correlate to the effective swelling ratio of the superabsorbent polymer in the pad (Table I). However, we find that this is not the case. Thus, the AUL test must apply additional stresses or perhaps variable stresses to the different polymer samples. This stress could be in the form of interparticle friction, which would vary with the particle shape and the number of particles. It is also well known that the AUL value of a given polymer usually decreases as the number of particles in the cell increases. In addition, granular materials are known to exhibit arching due to stress chains in the granular bed.

The data in Table I show that the polymer-only AUL values differ significantly over this set of samples. Furthermore, the AUL values on superabsorbent polymers do not correlate with the respective Q_{max} values. To see if the polymer-only AUL values are indicative of the swelling of the polymers in a pad under load, the pad AUL values under a compression of 0.6 psi are compared to the polymer AUL values under 0.6 psi. This is shown in Figure 11, from which we see that there is poor correlation between the polymer AUL and the pad AUL. In fact, for a group of 20 data pairs,
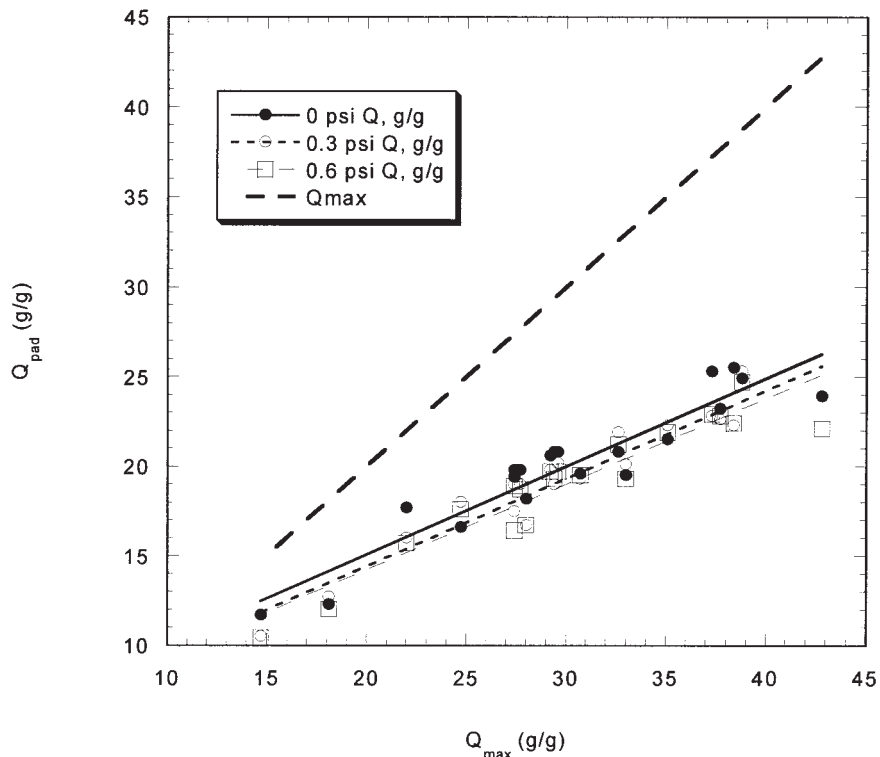
Figure 10 The swelling of superabsorbent polymers in pads at different compressive loads.

the coefficient of determination ($r^2 = 0.135$) indicates there is no statistically valid relationship between these quantities.

Differences in the ratio of gel swelling in pads can be most simply related to differences in the average crosslink density of the superabsorbent polymers, as measured by Q_{max}. For polymers at a given value of Q_{max}, there is no practical difference in the gel swelling ratio in composite pads under different body loads. The value of the polymer AUL has a poor correlation to the results in pads. However, we know that different polymers behave differently in diaper use tests and that the polymer AUL has been a somewhat useful guide for superabsorbent polymer development in the past 15 years. How can we bring together these apparently disparate data and interpretations? Simple, visual observations of swollen pads under a body load are useful.

In this work, we observe differences in the apparent pad wetness when using polymers with the same value of Q_{max} but a different gel modulus. These differences were observed during pad swelling under a body load with identical, limited volumes of saline solution added to the pad. Examples are shown in Figure 12. In addition to having identical values of Q_{max}, the polymers have the same value of Q_{pad} under a body load of 0.6 psi. The amount of liquid unabsorbed by the polymer is the same. However, pad A shows noticeable wetness at the edge of the pad whereas pad B appears to have a very dry edge. These differences are attributable to the differences in the gel modulus of the polymer in the pads.

Higher gel modulus yields a larger porosity in the pad compared to a pad of similar composition but with a smaller gel modulus. As a result of the higher pore volume, a given volume of unabsorbed liquid yields a lower saturation in the fiber mass, hence a drier composite. A possible value of the polymer-only
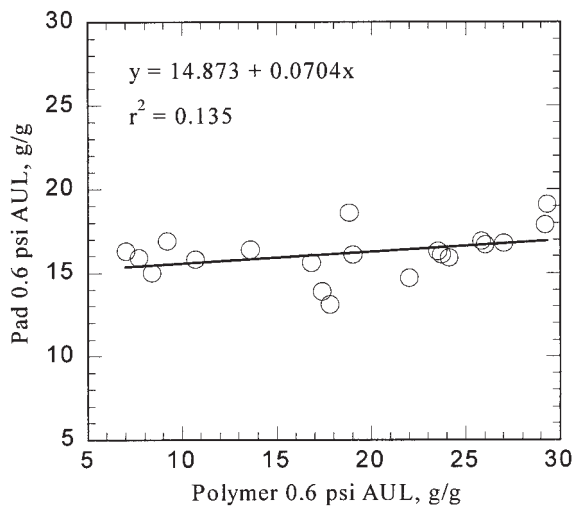

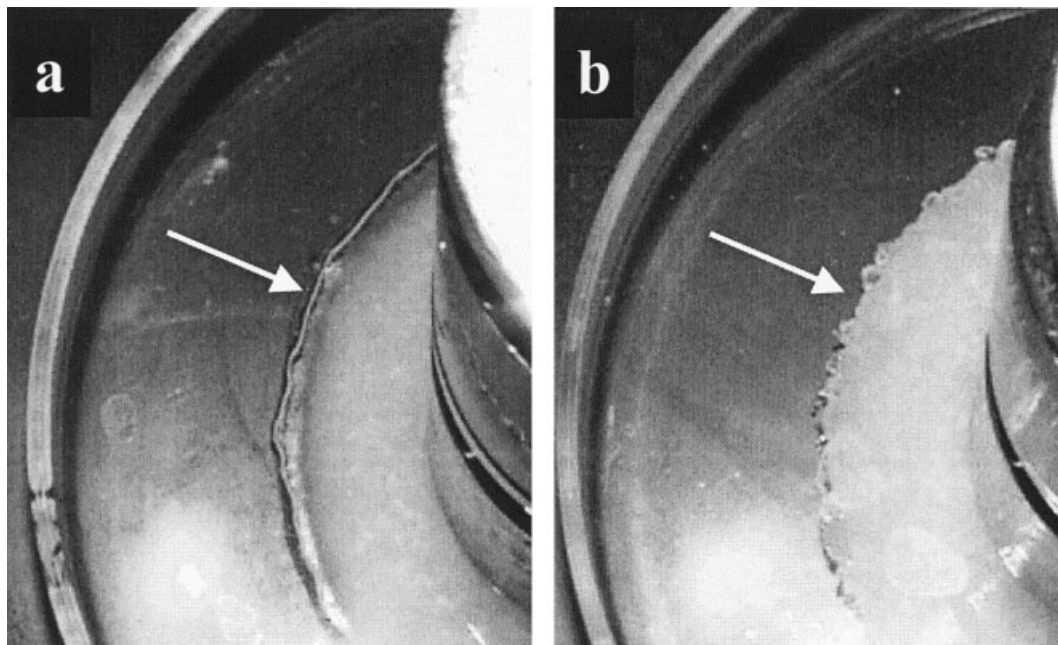**Figure 11** The pad versus polymer absorbencies under load.

Figure 12 Visualization of the pads under load. Wetness differences can be seen at the arrow positions: (a) fundamental superabsorbent polymer B, saturated, equilibrium swelling ratio = 37.9, G' (20 g/g) = 2.17 kPa; (b) fundamental superabsorbent polymer C, saturated, equilibrium swelling ratio = 38.5, G' (20 g/g) = 4.09 kPa.

AUL may be that, over a certain range, it gives a rough idea of the gel modulus of the sample. However, we show here that the actual value of the AUL bears no relationship to the swelling ratio of the polymer in a composite; hence, it is a misleading value.

CONCLUSION

We measured four sources of deswelling stress for superabsorbent polymers in composites that were not immersed in liquid. These were an extra Donnan exclusion of salt, capillary tension exerted by small fiber pores, compressive stress exerted by the fiber structure itself, and osmotic effects of soluble polymer leached from the superabsorbent polymer. Representative values of the stresses in a nonsaturated pad are summarized in Table V.

Because of the Donnan effect measured here, the higher gel swelling at low crosslink density must be

TABLE V
Representative Values of Deswelling Stresses in Pads

Source of stress	Equivalent deswelling pressure	
	kPa	psi
Ion exclusion/increased salt concn	2.10	0.30
Extractable polymer	0.83	0.12
Fiber compression	2.50	0.38
Capillary tension	0.64	0.093

accompanied by a larger absolute amount of unabsorbed liquid in the composite, leading to a wetter composite. Higher gel modulus improves the dryness of the composite by generating more pore volume per gram of gel, resulting in a lower degree of saturation of the composite. The polyelectrolyte nature of the superabsorbent polymer causes salt to accumulate in the unabsorbed liquid in a composite. This feature of superabsorbent polymers is not operative in the standard method for measuring the swelling capacity of superabsorbent polymers. As a result, the centrifuge retention capacity overestimates the ability of superabsorbent polymers to swell in the presence of limited amounts of liquid. This Donnan effect with limited liquid volume causes about 15% lower swelling than measured by the saturated, equilibrium swelling ratio. A useful design guide for superabsorbent polymer swelling in pads is 85% of the measured saturated, equilibrium swelling ratio.

When in the presence of cellulose fluff, the superabsorbent polymer swelled even less because the fiber exerts a compressive force on the superabsorbent polymer as it changes volume during swelling. The compression provided by the fiber network was about 0.3 psi, but it depends on the fiber to superabsorbent polymer ratio and the swelling ratio. A high volume fraction of gel reduces the magnitude of this effect. The shear modulus of the polymer did not appear to affect this phenomenon. The effect can be modeled in terms of a percolation concept based

on the wet fiber mass fraction in the swollen composite.

When the composite is not immersed in liquid, the pores between the fibers exert an additional capillary tension on the swelling polymer. This capillary tension of wet fiber reduces the superabsorbent polymer swelling by 10–20% more from the saturated, equilibrium swelling ratio value, depending on the saturation degree of the interfiber pores. The best superabsorbent polymers to overcome the capillary tensions are those swollen the least, either by virtue of a high crosslink density or by a larger polymer loading in the composite. High loading of more highly crosslinked superabsorbent polymer improves pad dryness because of the resulting high osmotic pressure of the gel phase and because of increased pore volume generated by swelling of the stiff gel.

In this work, we found that the AUL measured on a superabsorbent polymer was not a predictor of the gel swelling in a composite structure. The AUL value measured on the polymer was also not a good measure or predictor of the absorbency of a composite under load (e.g., pad AUL). A ratio of the AUL value to the saturated, equilibrium swelling ratio value was only a crude measure of the gel modulus, and it was not a good measure or predictor of the pore volume generated in a composite during swelling or of the compressibility of the swollen pad.

The soluble polymer content had a large negative effect on the swelling of superabsorbent polymers when swollen in a limited amount of saline solution. Roughly one-quarter of the available soluble polymer migrated from the gel in 1 h when the polymer sample was insulted with 1 equiv of saline solution. The result was about 5–7% less swelling than if no extractables were present. In addition to the deswelling effect, the 1% solution of polyacrylate reduced subsequent wicking by virtue of its higher viscosity.

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